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# General Principles and Processes of Isolation of Elements

# **OVERVIEW**

- 1. The most abundant element in the earth's crust is oxygen.
- 2. The most abundant metal in the earth's crust is aluminium.
- 3. The most abundant transition metal in the earth's crust is iron.
- 4. The earth's crust is the biggest source of metals. Metals occurs in nature in (i) native and (ii) combined states.
- Natural substances in which metals or their compounds occur in earth are called minerals. Minerals from which metals can be conveniently and economically extracted are called ores.
- 6. All ores are minerals, but all minerals are not ores.
- 7. Ores may be classified as
  - a. Native ores
  - **b.** Combined ores oxides, halides, sulphides etc.
- **8.** The process of extraction of the metal (in the pure form) from its ore is called **metallurgy**.
- **9.** Various steps involved in the extraction of a metal from its ores are as follows:
  - a. Grinding and pulverising the ore.
  - **b.** Concentration of the ore or ore-dressing.
  - c. Reduction of concentrated ore to the crude metal.
  - d. Refining of the crude metal.
- 10. The unwanted impurities, e.g. clay, associated with the ore are known as gangue or matrix.
- 11. Concentration of the ore or ore dressing is the process of removal of gangue from the ore.
- 12. Depending on the nature of the ore, ore-dressing is done by:
  - a. Hand picking
  - b. Hydraulic washing or gravity separation method: Native ores of Au, Ag, etc. and oxide ores of iron and tin are concentrated by this process.
  - c. Electromagnetic separation method: This method is used when either the impurities or ore are magnetic in nature. For example,
    - i. Chromite ore (magnetic) is separated from non-magnetic siliceous impurities.
    - ii. Wolframite ore (magnetic) (FeWO<sub>4</sub>) is separated from non-magnetic cassiterite ore (SiO<sub>2</sub>).

- d. Froth flotation process: Used for concentration of sulphide ores. The process is based on preferential wetting of ore particles by oil and gangue particles by water
- e. Leaching: Involves treating the ore with a suitable reagent to make it soluble while impurities remain insoluble. For example, native ores of Ag and Au are treated with NaCN in the presence of oxygen.
- 13. Reduction of the concentrated ore to the crude metal involves:
  - **a.** Conversion of the ore into metallic oxide by either calcination or roasting.
  - b. Reduction of metallic oxide to free metal by:
    - i. Smelting or pyrometallurgy: It is applicable mainly for the extraction of less electropositive metals such as Fe, Zn, Sn, Pb etc. by using C, CO, and Al as reducing agents.
    - ii. Reduction of Al: Goldschmidt aluminothermic process is used in case of those metals that have very high melting points and are to be extracted from their oxides.
    - iii. Self or auto-reduction process: The sulphide ores of less electropositive metals are heated in air so as to convert a part of the ore into oxide or sulphate, which further reacts with remaining sulphide ore to give metal and SO<sub>2</sub>.
    - iv. Electrolytic reduction: Highly electropositive metals such as alkali metals are extracted by the electrolysis of hydroxides, chlorides or oxides in the fused state.
    - v. Hydrometallurgy.
- 14. Basic concepts of thermodynamics is quite useful in selecting a suitable reducing agent for a particular oxide. In the oxidation reduction reaction,  $\Delta_j G^{\odot}$  should be negative at appropriate temperatures.

$$\Delta_t G^{\Theta} = \Delta_t H^{\Theta} - T \Delta_t S^{\Theta}$$

The concept is graphically displayed by  $-\Delta_f G^{\odot}$  vs T (in K) plots, i.e. Ellingham diagram.

**15. Purification or refining:** Process of purifying impure metals is called refining. It can be done by:

### 1.2 Inorganic Chemistry

- **a. Physical methods:** Liquation, distillation, zone refining, vacuum arc furnace refining etc.
- b. Chemical methods: Pyrometallurgical oxidation, electrolytic refining, vapour phase refining-Mond's or Van Arkel method, chromatographic separation, ion exchange methods, solvent extraction methods, Parting's process etc.

### 16. Furnaces:

- a. Reverberatory furnace: Used for roasting, smelting
- **b.** Muffle furnace: Used when high temperature is required.
- **c. Blast furnace:** Temperature at bottom is 1500°C and at the top is 200–300°C.

# d. Electric furnace:

- i. Arc furnace: Temperature ranges from 3000 to 3500°C.
- ii. Resistance furnace: Temperature ranges from 3000 to 4000°C.
- iii. Induction furnace: Temperature is 3000°C.

- 17. Many of the metals/non-metals are found in traces in living organisms, for example
  - a. Iron is found in haemoglobin.
  - b. Sodium in blood.
  - c. Magnesium in chlorophyll.
  - d. Mn, Fe and Cu in chloroplast.
  - e. Zn in eyes of cows and cats.
  - f. Cr in prawns.
  - g. Ca in bones.
  - h. Vanadium in cucumbers.
  - Iodine in sea weads.
- 18. Active metals like Li, Na, K, Ca, Mg, Sr, Ba etc. are obtained by the electrolysis of their fused chlorides, oxides or hydroxides.
- 19. Noble metals like Au, Ag etc. are obtained by cyanide or amalgamation process.
- 20. Heavy metals like Cu, Zn, Fe, Pb etc. are obtained by roasting and smelting process.
- 21. Thomas slag is  $Ca_3(PO_4)_2$ .
- 22. A mixture of iron oxide (Fe<sub>2</sub>O<sub>3</sub>) and Al powder in the ratio 3:1 is called **thermite mixture**. A mixture of Mg powder and BaO<sub>2</sub> is called **ignition powder**.

# 1.1 ABUNDANCE OF ELEMENTS IN THE EARTH'S CRUST

Earth's crust is made up of light elements, such as oxygen, silicon and aluminium. Oceanic crust is mostly basalt (which also contains magnesium and iron). Continental crust is composed of two main types of igneous rocks.

- 1. Light rocks, i.e. granite and related types (containing 70% SiO<sub>2</sub> together with Al<sub>2</sub>O<sub>3</sub>).
- Heavy rocks, i.e. basalt (containing 40–50% SiO<sub>2</sub> together with MgO).

Al is the second most abundant element in light rocks, and Mg is the second most available element in heavy rocks.

The relative abundance of elements in the earth's crust varies from one element to other and is given in Table 1.1.

**Table 1.1** Relative abundance of elements in the earth's crust

Element	Symbol	Atomic number	Abundance (%)
Oxygen	O	8	49.6
Silicon	Si	14	25.8
Aluminium	Al	13	7.4
Iron	Fe	26	4.6
Calcium	Ca	20	3.4
Sodium	Na	11	2.6
Potassium	K	19	2.4
Magnesium	Mg	. 12	1.9
Hydrogen	Н	1	0.9
Titanium	Ti	22	0.6
Chlorine	Cl	17	0.2
Phosphorous	P	15	0.1

**Note:** Together, these elements constitute 99.5% of earth's crust and the remaining elements total 0.5%.

#### ILLUSTRATION 1.1

Give examples of (a) igneous and (b) sedimentary rocks. What is the origin of (a) igneous rocks and (b) sedimentary rocks?

### Sol.

- (a) Example of igneous rock is granite.
- (b) Examples of sedimentary rock are chalk, sandstone, limestone.
- (a) **Origin of igneous rocks:** Solidified matter from magma on cooling forms igneous rocks.
- (b) Origin of sedimentary rocks: Sediments brought by rain or wind and deposited in rivers and lakes form sedimentary rocks.

# ${\sf l.1.1}$ Ocean as Source of Elements

Oceans are a rich source of many useful substances. Sea water, for xample, contains nutrients and minerals. Oil and natural gas occur continental shelf sediments. Metals such as gold and manganese

are found in sediments on the ocean floor. Sea water receives many of the dissolved salts by way of weathering of the earth's surface by rain water. This can be depicted by the following example:

Igneous rock + Rain water --- Stream of water + Detritus clay

$$CaAlSi_2O_8$$
  $[H_2O + CO_2]$  (Clay +  $SiO_2$ )

(Calcium aluminosilicate)

 $(Ca^{2+}, K^{\oplus}, Na^{\oplus}, HCO_3^{\ominus})$ 

KAlSi<sub>3</sub>O<sub>8</sub> (K aluminosilicate),

NaAlSi<sub>3</sub>O<sub>8</sub> (Na aluminosilicate).

Marine organisms convert  $\operatorname{Ca}^{2+}$  ions into  $\operatorname{CaCO}_3$  (shells), which forms sediments. Hydrochloric acid ejected by undersea volcanoes reacts with  $\operatorname{HCO}_3^{\Theta}$  to form chlorides of Na, K and Ca in sea water. A few elements such as chlorine, bromine, sodium and magnesium are recovered from sea water. Also some rare metals are recovered from manganese nodules, which are occasionally found in seabed.

Vast quantities of metallic salts are also held in solution in the oceans, the principal ions being Na $^{\oplus}$ , Mg $^{2+}$ , Ca $^{2+}$ , K $^{\oplus}$ , Sr $^{2+}$ , Cl $^{\ominus}$ , SO $_4^{2-}$ , HCO $_3^{\ominus}$ , F $^{\ominus}$ , Cl $^{\ominus}$ , and Br $^{\ominus}$ . In the future, sea water may become an important source of many metals such as uranium and gold.

# 1.2 MODES OF OCCURRENCE OF ELEMENTS

Elements occur in nature either in the fresh (uncombined or native) state or in the combined state (as compounds). The reason for difference in mode of occurrence is difference in chemical reactivities.

#### 1.2.1 NATIVE STATE

When an element is found free or in uncombined state, it is said to occur as native. These elements have little or no affinity for oxygen and resists the attack of water and other chemical reagents. Some elements found in the native state are copper (Cu), silver (Ag), gold (Au), mercury (Hg), platinum (Pt) etc.

# 1.2.2 COMBINED STATE

Elements which easily react with oxygen, moisture and other chemical reagents occur in the combined state, i.e. in form of their compounds. In the combined state, non-metals occur in the reduced form, i.e.,  $X^{\Theta}$  (where  $X^{\Theta} = F^{\Theta}$ ,  $Cl^{\Theta}$ ,  $Br^{\Theta}$ , etc.), whereas metals occur in the oxidised form i.e., oxides (e.g.  $Al_2O_3$ ,  $Fe_2O_3$ ) etc.

# 1.3 MODE OF OCCURRENCE OF METALS

The naturally occurring materials in which metals or their compounds occur in the earth's crust are called **minerals**. Those minerals from which the metals may be extracted conveniently and economically are called ores.

All ores are minerals, but all minerals are not ores. For example, all clays contain aluminium but clay ( $Al_2O_3 \cdot 2H_2O$ ) is not considered an ore of aluminium, since the extraction of Al from clay is neither convenient nor economically viable. Thus, clay is an example of mineral. Whereas bauxite ( $Al_2O_3 \cdot 2H_2O$ ) is considered a ore or aluminium, since aluminium can be conveniently and economically extracted from bauxite.

# 1.3.1 CLASSIFICATION OF ORES

Based on their mode of occurrence, ores are classified as follows:

- 1. Native ores: These ores contain metals in the free state. Sometimes, lumps of almost pure metals are also found, which are known as **nuggets**.
  - Examples of native ores are copper (Cu), silver (Ag), and platinum (Pt).
- 2. Combined ores: These ores have metals occurring in simple or complex form as follows:

	Types o	f Name of the or		
	ore		of the ore	
1. Oxides		Corundum	$Al_2O_3$	
		Diaspore	$Al_2O_3\cdot H_2O$	
		Bauxite	$Al_2O_3 \cdot 2H_2O$	
		Tin stone	SnO <sub>2</sub>	
		Rutile	TiO <sub>2</sub>	
		Haematite	$Fe_2O_3$	
		Magnetite	$Fe_3O_4$	
		Limonite	$Fe_2O_3 \cdot 3H_2O$	
		Chromite	FeO·Cr <sub>2</sub> O <sub>3</sub>	
		Cuprite (or ruby	$Cu_2O$	
		copper)		
		Illmenite	FeO·TiO <sub>2</sub>	
		Zincite	$ZnO_2$	
		Pyrolusite	$MnO_2$	
2.	Sulphides	Galena	PbS	
		Zinc blende	ZnS	
		Cinnabar	HgS	
		Argentite	$Ag_2S$	
		(or silver glance)		
		Pyrargyrite	$3Ag_2S \cdot Sb_2S_2$	
		(or ruby silver)		
		Iron pyrites	FeS <sub>2</sub>	
		Copper pyrites	CuFeS <sub>2</sub> or Cu <sub>2</sub> S·Fe <sub>2</sub> S <sub>3</sub>	
		Chalcocite	Cu <sub>2</sub> S	
		(or copper	,	
		glance)		
3.	Halides	Rock salt	NaCl	
		Horn silver	AgCl	
		Carnallite	KCl·MgCl <sub>2</sub> ·6H <sub>2</sub> O	
		Fluorspar	CaF <sub>2</sub>	
		Cryolite	Na <sub>3</sub> AlF <sub>6</sub>	
4.	Control	Sylvine	KCl	
4.	Carbonates	Magnesite	MgCO <sub>3</sub>	
	,	1	CaCO <sub>3</sub>	
		Dolomite	CaCO <sub>3</sub> ·MgCO <sub>3</sub>	
		Calamine	ZnCO <sub>3</sub>	
		Malachite	CuCO <sub>3</sub> ·Cu(OH) <sub>2</sub>	
			Cu(OH) <sub>2</sub> ·2CuCO <sub>3</sub>	
			PbCO <sub>3</sub>	
			3	
		Sidelife	FeCO <sub>3</sub>	

	G. 1. 1tog	Epsom salt	$MgSO_4 \cdot 7H_2O$
5	. Sulphates	or epsomite	11120
		Barytes	BaSO <sub>4</sub>
		Gypsum	CaSO <sub>4</sub> ·2H <sub>2</sub> O
		Glauber's salt	Na <sub>2</sub> SO <sub>4</sub> ·10H <sub>2</sub> O
		Kainite	KCl.MgSO <sub>4</sub> ·3H <sub>2</sub> O
		Calestine	SrSO <sub>4</sub>
		Chalcanthite	CuSO <sub>4</sub> ·5H <sub>2</sub> O
		Anglesite	PbSO <sub>4</sub>
		Anhydrite	CaSO <sub>4</sub>
6.	Silicates	Petalite	$LiAl(Si_2O_5)_2$
			(All are ores of Li)
		Beryl	3BeO·Al <sub>2</sub> O <sub>3</sub> ·6SiO <sub>2</sub>
			(All are ores of beryllium)
		Willemite	Zn <sub>2</sub> SiO <sub>4</sub>
		China clay	Al <sub>2</sub> O <sub>3</sub> ·2SiO <sub>2</sub> ·2H <sub>2</sub> O
		Mica	$K_2O \cdot 3Al_2O_3 \cdot 6SiO_2 \cdot 2H_2O$
		Felspar	KAlSi <sub>3</sub> O <sub>8</sub>
	1	1	or K <sub>2</sub> O·Al <sub>2</sub> O <sub>3</sub> ·6SiO <sub>2</sub>
		Talc	$Mg_2(Si_2O_5)-Mg(OH)_2$
		Asbestos	CaMg <sub>3</sub> ·(SiO <sub>3</sub> ) <sub>4</sub> or
			CaSiO <sub>3</sub> ·3MgSiO <sub>3</sub>
7.	Phosphates	Amblygonite	LiF·AlPO <sub>4</sub>
		Triphylite	(Li, Na)PO <sub>4</sub> ·(Fe, Mn) <sub>3</sub> (PO <sub>4</sub> ) <sub>3</sub>
		Chlorapatite	$Ca_3(PO_4)_3C1$
		Fluorapatite	3Ca <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub> CaF <sub>2</sub>
8.	Nitrates	Saltpetre	KNO <sub>3</sub>
		Chile saltpetre	NaNO <sub>3</sub>
9.	Arsenides	Kupfernickel	NiAs
		Nickel glance	NiAsS

#### ILLUSTRATION 1.2

- **a.** In general, which metals are expected to occur in the native state in nature?
- b. A certain metal M occurs in three compounds namely X, Y and Z. X has 15% of M, Y has 66% of M and Z has 71% of M. If we extract M from X, Y and Z, it costs Rs. 35 per kg, Rs. 45 per kg and Rs. 100 per kg respectively. Out of X, Y and Z which mineral can be considered as an ore of M?

#### Sol.

- a. The elements which lie below hydrogen in the electrochemical series are expected to occur in the nature in the native state. For example, Cu, Ag, Au, Pt etc.
- b. All three X, Y and Z are minerals as they contain M, but all cannot be called ores. Extraction of M from mineral X would cost less but result in a very less amount. Similarly, extraction from Z would result in large amount, but it will also cost a large sum. Hence Y is the appropriate mineral from which M should be extracted as it would give sufficient amount and would not even cost much.

# 1.3.2 FACTORS ON WHICH MODE OF **OCCURRENCE DEPENDS**

Mode of occurrence depends on the following factors:

1. Enthalpy of formation

2. Electrode potential

3. Size, charge, polarisability—HSAB principle

1. Enthalpy of formation  $(\Delta_c H^{\Theta})$ : Standard enthalpy of formation for some compounds of calcium is as follows:

Compound	$\Delta_f H^{igotimes}(\mathrm{kJ\ mol}^{-1})$	Ore
$Ca_3(PO_4)_2$	-4126	Phosphorite
CaF <sub>2</sub>	-1214	Fluorspar
CaCO <sub>3</sub>	-1207	Calcite
CaCl <sub>2</sub>	-795	_
CaO	-635	_
CaS	-483	

For a compound to exist as mineral, it should be stable, i.e. should not be attacked by moisture, O2 or CO2. The compound should be thermally stable. Considering the value of  $\Delta_t H^{\Theta}$ , the probability of finding Ca as calcium phosphate is maximum. CaCl<sub>2</sub>, CaO, CaS do not occur as they are not stable towards water. But it is not always possible that a compound which is maximum stable should occur in nature, as will be discussed later on. Even if a very stable compound is present, it may not be profitable to use it as an ore. Because if it very stable, it is difficult to extract metal from that compound.

Ele-			$\Delta_f H^{\Theta}$ (kJ mol $^{-1}$ )			
ment	Car- bonate	Chloride	Oxide	Sul- phide	Ores	
Na	-1131	-411	-416	-373	NaCl (Rock salt)	
Al	_	-695	-1669	-509	Al <sub>2</sub> O <sub>3</sub> ·2H <sub>2</sub> O (Bauxite)	
Zn	-812	-416	-348	-203	ZnCO <sub>3</sub> (Zinc blende)	
Fe	-748	-405	-822	-178	Fe <sub>2</sub> O <sub>3</sub> (Haematite)	
Au	- 1	+118	+80.8	- 4	Free state	

Na should occur in nature as Na2CO3, as it is most stable, but it occurs as NaCl because of the conditions in nature. Al occurs as alumina as its oxide is most stable, and Al is extracted from this compound. Au cannot occur in nature in the combined state due to the high positive value of  $\Delta_f H^{\odot}$ . Hence Au compounds are not stable.

2. Electrode potential:  $E^{\Theta}$  value of H is 0.0V. In the emf series, the elements above H are electropositive. They can replace H from the acidic solution, hydrogen gas from water. They are easily converted to ions.

$$Na^{\oplus} + e^{\ominus} \longrightarrow Na$$

$$E_{\rm red}^{\Theta} = -2.71 \text{ V}$$

 $Na^{\oplus} + e^{\Theta} \longrightarrow Na$   $E_{red}^{\Theta} = -2.71 \text{ V}$ This value shows that the moment Na comes in contact with

water, 
$$H_2$$
 gas is liberated.  
 $Na + H_2O \longrightarrow NaOH + \frac{1}{2}H_2$ 

Therefore, Na cannot exist in free state in native. Au can exist in free state because Au cannot replace H<sub>2</sub> from H<sub>2</sub>O, as it lies below H in the emf series. Similarly, Cu and Ag also occur in nature in native state. By making use of standard electrode potentials, it is inferred that

a. Highly electropositive metals are those for which standard electrode potential value is less than or equal to -2.3 V, with reference to the following reaction:

$$M_{(aq)}^{n+} + ne^{\Theta} \longrightarrow M_{(s)}$$
  $E^{\Theta} \le -2.3 \text{ V}$  or example,

	Li <sup>⊕</sup> /Li	K <sup>⊕</sup> /K	Ba <sup>2+</sup> /Ba
$E^{\Theta}(V)$	-3.04	-2.92	-2.90
MAL PROPERTY	Ca <sup>2+</sup> /Ca	Na <sup>⊕</sup> /Na	Mg <sup>2+</sup> /Mg
$E^{\Theta}(V)$	-2.87	-2.71	-2.37

b. Moderately electropositive metals have standard electrode potential value between -0.44 V and -2.3 V.

For example,

	A1 <sup>3+</sup> /A1	Ti <sup>2+</sup> /Ti	Mn <sup>2+</sup> /Mn
$E^{\Theta}(V)$	-1.66	-1.63	-1.16
Selevions	$Zn^{2+}/Zn$	Fe <sup>2+</sup> /Fe	: 1
$E^{\Theta}(V)$	-0.76	-0.44	

c. Weak or very weak electropositive metals having standard reduction potential values greater than -0.44 V.

For example,

	Ni <sup>2+</sup> /Ni	Pb <sup>2+</sup> /Pb	Cu <sup>2+</sup> /Cu
$E^{\Theta}(V)$	-0.25	-0.13	+0.34
	Ag <sup>⊕</sup> /Ag	Au <sup>3+</sup> /Au	
$E^{\Theta}(V)$	-0.80	+1.5	

From the above values, it can be inferred that Cu, Ag and Au can exist in nature in free state.

Another aspect of  $E^{\Theta}$  value is to predict probable oxidation state of a particular metal amongst the others under similar conditions. Only that oxidation state is possible which is thermodynamically stable.

- 3. HSAB principle: Mode of occurrence of metals in a particular compound can also be predicted by using Hard Soft Acid Base (HSAB) principle. Soft acids form stable compounds with soft bases, while hard acids form stable compounds with hard bases. Borderline acids, i.e., metals in between hard acids and soft acids have preference for both soft and hard bases. For
  - **a.**  $Ca^{2+}$ ,  $Mg^{2+}$ ,  $Ti^{4+}$  and  $Al^{3+}$  occur as  $CaCO_3$ ,  $MgCO_3$ ,  $TiO_2$ , and  $Al_2O_3$ , respectively.  $Ca^{2+}$ ,  $Mg^{2+}$ ,  $Ti^{4+}$ , and  $Al^{3+}$  are hard acids, while  $CO_3^{2-}$  and  $O^{2-}$  are hard bases.
  - **b.**  $Cu^{2^+}$ ,  $Ag^{\oplus}$  and  $Hg^{2^+}$  occur as sulphides namely CuS, AgS, and HgS since  $Cu^{2^+}$ ,  $Ag^{\oplus}$  and  $Hg^{2^+}$  are soft acids, while  $S^{2-}$  is a soft base.

# 1.4 EXTRACTION OF ELEMENTS

As already discussed, very few elements occur in the native state in nature. In the combined state, metals are usually found in the oxidised form (e.g., Fe2O3, MnO2, SnO2) while non-metals are present in the reduced form such as  $X^{\Theta}(X^{\Theta} = Cl^{\Theta}, Br^{\Theta}, I^{\Theta})$ . The methods of extraction or isolation of metals and nonmetals from natural sources are, therefore, quite different. Metals have to be free from their oxidised forms by reduction, while non-metals are obtained by oxidation. Their extractions are accordingly treated separately here. Reduction is brought about by electronation, i.e. by providing electron directly or indirectly, while oxidation is carried out by de-electronation i.e. by removing electron, directly or indirectly.

### 1.4.1 EXTRACTION OF NON-METALS

Non-metals occurring in the combined form are generally extracted by oxidation. Among non-metals, halogens are most important. Consider, for example, the oxidation of  $Cl^{\Theta}$  ions in water:

$$2 \text{ Cl}^{\Theta}_{(aq)} + 2\text{H}_2\text{O}_{(l)} \longrightarrow 2 \text{ OH}^{\Theta}_{(aq)} + \text{H}_{2(g)} + \text{Cl}_{2(g)}$$

The oxidation of  $Cl^{\Theta}$  ions to chlorine cannot be brought about by ordinary chemical methods. The oxidation of  $Cl^{\Theta}$  is accomplished by electrolysis. The minimum potential difference required for this is 2.2 V. Similarly, fluorine is also extracted by electrolysis. Elements like oxygen, nitrogen and noble gases are available from air. Carbon, sulphur and phosphorus are extracted either from native ores or by oxidation from their compounds occurring in nature. Since there is no general method of extraction of non-metals individual cases will be considered at the appropriate places in the text.

# 1.4.2 EXTRACTION OF METALS—METALLURGY

Metals are usually extracted from their ores by reduction processes, except in cases where the metals are unreactive ones. Before an ore is subjected to reduction, it needs to be subjected to various other processes/operations, such as concentration, calcination, etc.

The process of extracting metals from their ores and refining them is called **metallurgy**. (as shown in Fig. 1.1)

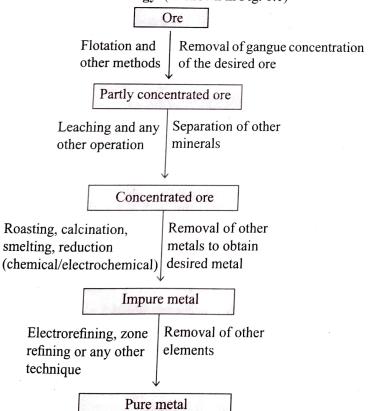


Fig. 1.1 Flow sheet for general metallurgical operation; the functions of processes are given on the right side, and the methods employed are given on the left

The process of extraction of a metal depends on the nature of the ore and chemical properties of the metal. Since different metals have different physical and chemical properties, the method of extraction varies from one metal to another. Hence, a single universal method cannot be applied for the extraction of all the metals. Different metallurgical operations are employed in the extraction of metals, and these are listed as follows:

- 1. Grinding and pulversing the ore.
- **2.** Concentration of the ore (ore-dressing).
- 3. Reduction of the concentrated ore to crude metal.
- 4. Refining of the crude metal.

Various methods are available for each of these stages. The choice of the method employed depends on the type of impurity present, type of the metal, available facility, etc. All these metallurgical operations are discussed as follows:

### 1.4.3 GRINDING AND PULVERISING

Ores as obtained from the earth's crust usually occur in the form of big lumps. These lumps are broken or crushed into small pieces by means of jaw crushers or grinders. The process is known as as grinding.

The small pieces thus obtained are reduced to fine powder with the help of ball mill or stamp mill. This process is known as **pulverisation**.

# 1.4.4 CONCENTRATION OF THE ORE (ORE-DRESSING)

Metallic ores as obtained from the earth's crust are often mixed with non-metallic and rocky materials such as clay, sand, limestone, etc. The impurities present in the metallic ores are called **gangue or matrix.** The process of removal of the gangue from the ore is called **concentration of the ore-dressing or benefaction process** and the purified ore is called **concentrate.** Some important methods for ore-dressing are as follows:

#### 1.4.4.1 Hand Picking

When the impurities present are quite distinct from the ore so that they can be easily differentiated by our eyes, picking by hand is done.

# 1.4.4.2 Hydraulic Washing or Gravity Separation Method

**Principle:** It is based on the difference in the specific gravity of the metallic ore and the gangue particles. This method is used mainly for heavier ores such as cassiterite (SnO<sub>2</sub>), haematite (Fe<sub>2</sub>O<sub>3</sub>).

Working: Powdered ore is treated with a stream of running water; gangue particles which are lighter (as compared to metallic ore) are washed away, while the heavier ore particles are left behind. This is known as levigation. Two common methods for hydraulic washing are as follows:

1. Wilfley table method: This process involves the use of sloping wooden table. The wooden table has a slanting floor on which long wooden strips called cleats as rifles are fixed. The crushed ore is fed onto the top of the table, which is kept vibrating all the time. A running water stream is made to flow across the table at right angles to the slope. The lighter siliceous and earthy gangue particles rise up and are carried away, while heavier particles settle at the bottom.

2. Hydraulic classifier method: Hydraulic classifiers (Figure 1.2) consists of a conical reservoir fitted with hopper at the top and pipe at the bottom. Powdered ore is dropped from the hopper and a powerful stream of water is forced in through the pipe below. Lighter gangue particles are carried away by the current of water and heavier ore particles collect at the apex of the cone. The conical shape helps in reducing the velocity of water and thus ore particles are prevented from being carried away by water.

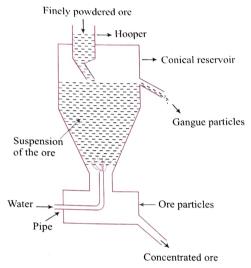


Fig. 1.2 Hydraulic classifier

# 1.4.4.3 Electromagnetic Separation Method

**Principle:** This method is based on magnetic and non-magnetic properties of the ore and gangue, respectively. This method can be used when the ore is magnetic (attracted by the magnet) and gangue is non-magnetic. This method can be used to separate:

- 1. Chromite, Fe(CrO<sub>2</sub>)<sub>2</sub>, from siliceous impurities. Chromite is magnetic, whereas siliceous impurities are non-magnetic.
- 2. Mixture of Wolframite (FeWO<sub>4</sub>) and cassiterite (SnO<sub>2</sub>). Wolframite is magnetic, whereas cassiterite is non-magnetic.
- 3. Mixture of rutile (TiO<sub>2</sub>) and chloroapatite, [CaCl<sub>2</sub>·3Ca<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>]. Rutile is magnetic, whereas chloroapatite is non-magnetic.

Working: This method involves the use of electromagnetic separator. The separator consists of leather or brass belt moving over two rollers, one of which encloses magnet in it. The powdered ore is dropped on this moving belt. The magnetic component gets attracted by the magnet and falls just below it, whereas the non-magnetic component falls away from it, as shown in Fig. 1.3.

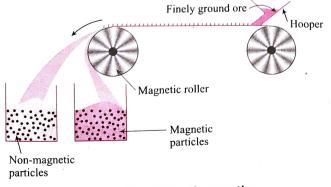


Fig. 1.3 Electromagnetic separation

#### 1.4.4.4 Froth Flotation Method

**Principle:** This method is based on different wetting characteristics of the ore and gangue by oil and water. Ore is preferentially wetted by oil, whereas gangue is preferentially wetted by water.

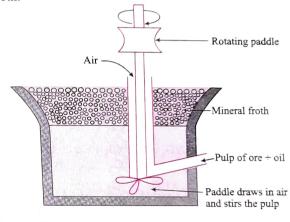
This method is extensively employed for concentration of sulphide ores, e.g., galena (PbS), copper pyrites (CuFeS<sub>2</sub>) and zinc blende (ZnS).

**Working:** A suspension of finely powdered ore with water is made. Depending on the nature of the ore, various additives such as frothers froth stabilisers and collectors are added to the above suspension.

Frothers such as pine oil help in the formation of froth.

Froth stabilisers such as cresols and aniline help in stabilising the froth.

Collectors such as ethyl xanthate, potassium ethyl xanthate, and fatty acids help in enhancing the non-wettability of the mineral particles. These attach themselves by polar groups to the grain of minerals, which then become water repellent and pass on to the froth.



showing mineral particles attached to it

Fig. 1.4 Froth flotation method

Enlarged view of an air bubble

A rotating paddle (Figure 1.4) agitates the suspension and draws in air causing the formation of the froth, which carries with it the mineral particle. The froth being lighter floats to the surface and is skimmed off. It is allowed to collapse and dry for recovery of mineral particles.

By adjusting the proportion of oil to water, it is often possible to separate one sulphide ore from another. One more additive, **depressants or activators**, is added to prevent certain type of sulphide ore particles from forming the froth with the bubbles. Thus, it helps in the separation of different minerals present in the same ore. For example, galena (PbS) is usually associated with zinc blende (ZnS). In this case, froth flotation process is carried out by using a depressant (NaCN).

NaCN (depressant) depresses the flotation property of ZnS and FeS<sub>2</sub> grains, so that PbS passes into the froth when air is blown in. This is due to the reason that NaCN reacts with ZnS, thus forming a zinc complex Na<sub>2</sub>[Zn(CN)<sub>4</sub>] on the surface of ZnS, thereby preventing it from forming the froth. Under these conditions, only PbS forms froth and hence is separated from ZnS ore.

 $ZnS + 4NaCN \longrightarrow Na_2[Zn(CN)_4] + Na_2S$ Sodium tetracyanidozincate (II)

# 1.4.4.5 Leaching or Hydrometallurgy

Principle: Leaching depends on the difference in chemical properties of the ore and gangue. Leaching involves the treatment of finely powdered ore with a suitable reagent (acids, bases or other chemicals), which can selectively dissolve the ore but not gangue. The metal is then recovered from its salt solution either by its electrolysis or by adding some electropositive metal to it when the metal to be extracted is obtained as a precipitate. Some important examples are described below:

1. Leaching of bauxite (Bayer's process): In Bayer's process, pure alumina (Al,O3) is obtained from the bauxite ore. Impurities usually associated with the bauxite ore are iron (III) oxide (Fe<sub>2</sub>O<sub>3</sub>), silica (SiO<sub>2</sub>) and titanium oxide (TiO<sub>2</sub>). The powdered ore is treated with concentrated solution of NaOH (45%) at 473-573 K. Al<sub>2</sub>O<sub>3</sub> dissolves forming sodium metaaluminate, and other impurities are left behind.

$$Al_2O_{3(s)} + 2NaOH_{(aq)} + 3H_2O_{(l)} \longrightarrow 2Na[Al(OH)_4]_{(aq)}$$
  
Sodium metaaluminate

or
$$Al_2O_{3(s)} + 2OH_{(aq)} + 3H_2O \longrightarrow [Al(OH)_4]_{(aq)}^{\Theta}$$

The solution containing sodium metaaluminate is filtered, and the filtrate is cooled and its pH is adjusted downward by dilution and/or neutralisation with carbon dioxide (CO2), when aluminium hydroxide [Al(OH)3] is precipitated. Seeding with a little freshly precipitated aluminium hydroxide quickens the process.

$$[\mathrm{Al}(\mathrm{OH})_4]^{\bigodot}_{(aq)} \xrightarrow{\mathrm{dilution}} \mathrm{Al}(\mathrm{OH})_{3(s)} + \overset{\bigodot}{\mathrm{OH}}_{(aq)}$$

The precipitate of Al(OH)<sub>3</sub> is filtered, dried and finally heated to about 1473K to obtain pure Al<sub>2</sub>O<sub>3</sub>.

$$2\text{Al(OH)}_{3(s)} \xrightarrow{1473 \text{ K}} \text{Al}_2\text{O}_{3(s)} + 3\text{H}_2\text{O}_{(g)}$$

2. Extraction of copper (Cu): Large heap of copper glance, Cu<sub>2</sub>S, is exposed to air and water. In about a year, the ore Cu<sub>2</sub>S is oxidised to CuSO<sub>4</sub>. The solution of CuSO<sub>4</sub> is either electrolysed or scrap iron is added to it to get Cu as precipitate.

$$2Cu_2S + 5O_2 \longrightarrow CuSO_4 + 2CuO$$

$$CuSO_4 + Fe \longrightarrow FeSO_4 + Cu \downarrow$$

3. Leaching of silver and gold ores (MacArthur and Forest's cyanide process): Leaching is also employed in concentrating silver and gold ores. In this process, the finely powdered ore argentite (Ag<sub>2</sub>S) or the native silver or gold is treated with dilute solution of NaCN or KCN and a current of air is continuously passed into the solution. As a result, the precious metals are converted into soluble complex. Thus,

$$4M + 8CN^{\odot} + 2H_{2(air)} \longrightarrow 4[M(CN)_2]^{\odot} + 4\overset{\odot}{OH}$$
Soluble complex
(where M = Ag or Au)

or
$$4M + 8NaCN + 2H2O + O2 \longrightarrow 4Na[M(CN)2] + 4NaOH$$

$$(M = Ag \text{ or } Au)$$

In case of ore argentite (Ag<sub>2</sub>S), the following reaction takes place:

$$Ag_2S + 4NaCN \Longrightarrow 2Na[Ag(CN)_2] + Na_2S$$

The above reaction is a reversible reaction, but when current of air is passed into the solution, Na2S formed in the above reaction

is oxidised to Na<sub>2</sub>SO<sub>4</sub>, hence the reaction proceeds in the forward

$$4Na_2S + 2H_2O + 5O_2 \longrightarrow 2Na_2SO_4 + 4NaOH + 2S$$
(air)

# 1.4.5 REDUCTION OF CONCENTRATED ORE TO THE **METALLIC OXIDE**

The concentrated ore needs to be converted into a form which is suitable for reduction to the metal. Metals are usually present in ores as hydroxides (hydrated oxide), carbonates or sulphides These ores are subjected to either calcination or roasting/smelting depending upon the nature of the minerals present in the ore, and thereby converted to the oxide form. For thermodynamic reasons it is easier to reduce an oxide than the sulphide ore.

### 1.4.5.1 Calcination

Calcination is the process in which the ore is heated strongly in absence or limited supply of air at a temperature that the ore does not melt. This ensures the removal of:

- 1. Volatile impurities such as moisture, CO<sub>2</sub>, SO<sub>2</sub>, organic matter  $2\text{Fe(OH)}_3 \xrightarrow{\Delta} \text{Fe}_2\text{O}_3 + 3\text{H}_2\text{O}\uparrow$
- 2. Water from hydrated ore

$$Al_2O_3 \cdot 2H_2O \xrightarrow{\Delta} Al_2O_3 + 2H_2O$$
Bauxite

3. Carbon dioxide from carbonate ore

$$\begin{array}{l} \text{CaCO}_{3} \xrightarrow{\Delta} \text{CaO} + \text{CO}_{2} \uparrow \\ \text{Limestone} \\ \text{CaCO}_{3} \cdot \text{MgCO}_{3} \xrightarrow{\Delta} \text{CaO} + \text{MgO} + 2\text{CO}_{2} \uparrow \end{array}$$

Calcination is usually done in reverberatory furnace. It makes the mass porous so that it can be easily reduced to metallic state in the next step of metallurgy.

### 1.4.5.2 Roasting

Roasting is a process in which the ore (usually sulphide) is heated strongly in presence of air, at a temperature below the melting point of the ore. This step ensures:

1. Conversion of the ore to the oxide form

$$2HgS + 3O_{2} \xrightarrow{\Delta} 2HgO + 2SO_{2}$$
Cinnabar
$$Cu_{2}S + 3O_{2} \xrightarrow{\Delta} 2Cu_{2}O + 2SO_{2}$$
Copper glance
$$2ZnS + 3O_{2} \xrightarrow{\Delta} 2ZnO + 2SO_{2}$$
Zinc blends

Sometimes, a part of the sulphide may act as reducing agent as in the case of extraction of lead.

$$2PbS + 3O_2 \longrightarrow 2PbO + 2SO_2$$
Galena
 $PbS + 2PbO \longrightarrow 3Pb + SO$ 

$$PbS + 2PbO \longrightarrow 3Pb + SO_2$$

Sometimes, insoluble sulphide ores are converted to corresponding sulphate ore, which are water soluble.

$$\begin{aligned} &\operatorname{CuS} + 2\operatorname{O}_2 \longrightarrow \operatorname{CuSO}_4 \\ &\operatorname{ZnS} + 2\operatorname{O}_2 \longrightarrow \operatorname{ZnSO}_4 \end{aligned}$$

2. Removal of non-metallic impurities such as arsenic (As), antimony (Sb), sulphur (S) and phosphorous (P), which are oxidised to oxides, as volatile gases.

$$4As + 3O_2 \longrightarrow 2As_2O_3 \uparrow$$

$$4Sb + 3O_2 \longrightarrow 2Sb_2O_3 \uparrow$$

$$S + O_2 \longrightarrow SO_2 \uparrow$$

$$P_4 + 5O_2 \longrightarrow P_4O_{10} \uparrow$$

- 3. Removal of water from hydrated ores.
- 4. Makes the ore porous so that it undergoes easier reduction in the next step of metallurgy.

Roasting is usually done in reverberatory furnace or blast furnace (Figure 1.5).

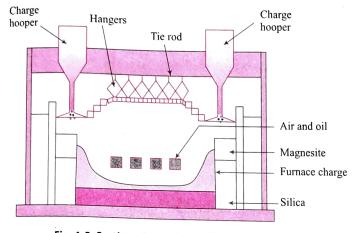


Fig. 1.5 Section of a modern reverberatory furnace

During roasting, air vents are kept open, whereas during calcination, air vents are either completely or partially closed.

# 1.4.6 REDUCTION OF ROASTED/CALCINED ORE TO METAL

The extraction of a metal from its oxide by a process involving melting is known as **smelting**. If the roasted/calcined ore still contains non-fusible impurities of earthy matter (such as silicasilicates, metallic oxides, etc.), an additional substance is added to the furnace charge (roasted/calcined ore and coke) during the process of smelting to remove them. This additional substance is known as **flux**.

During smelting, flux combines with non-fusible impurities (gangue) and forms **slag**, a fusible material.

$$Flux + Gangue \longrightarrow Slag$$

Slag, being lighter than molten metal, floats on the molten metal, from where it can be easily removed. At high temperature, slag is a liquid, which is insoluble in the molten metal.

Types of fluxes: Fluxes are of two types:

1. Acidic fluxes: Acidic fluxes such as silica (SiO<sub>2</sub>) and borax (Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub>·10H<sub>2</sub>O) are added to the basic impurities, such as, metallic oxides (such as CaO, FeO), hence removing them as fusible slag.

Acidic flux + Basic impurity 
$$\longrightarrow$$
 Fusible slag  
SiO<sub>2</sub> + CaO  $\longrightarrow$  CaSiO<sub>3</sub>

$$SiO_2 + FeO \longrightarrow FeSiO_3$$

Basic fluxes: Basic fluxes such as limestone (CaCO<sub>3</sub>),
magnesite (MgCO<sub>3</sub>) and haematite (Fe<sub>2</sub>O<sub>3</sub>) are added to
remove acidic impurities such as silica (SiO<sub>2</sub>) as fusible slag.

Basic flux + Acidic impurity 
$$\longrightarrow$$
 Fusible slag  
 $MgCO_3 + SiO_2 \longrightarrow MgSiO_3 + CO_2 \uparrow$   
 $CaCO_3 + SiO_2 \longrightarrow CaSiO_3 + CO_2 \uparrow$ 

In general, most of the metals which occur in the combined state are present in their positive oxidation states. They must therefore be reduced by electronation, providing electrons to become free metals. The nature of reducing agent to be used in a particular case depends on how difficult the reduction process is. If the metal is very reactive like the alkali metals, alkaline earth metals and aluminium, they can be reduced only by the electrolytic method. Less reactive metals such as copper, lead, tin, etc. can be reduced by chemical reducing agents. The choice of the reducing agent is decided by the factors of energetics and economics. Various reduction processes are described as follows:

- 1. Chemical reduction
- 2. Auto-reduction or self-reduction
- 3. Electrolytic reduction

# 1.4.6.1 Chemical Reduction

Carbon as reducing agent: Carbon can be used as reducing agent for extraction of lead (Pb), zinc (Zn), copper (Cu), tin (Sn). Roasted oxide ore is mixed with carbon (charcoal, coke or coal) and a flux and heated to a high temperature in a suitable furnace.

Metal oxide + C  $\xrightarrow{\Delta}$  Metal + Carbon monoxide

PbO + C 
$$\xrightarrow{\Delta}$$
 Pb + CO  
Fe<sub>2</sub>O<sub>3</sub> + 3C  $\xrightarrow{\Delta}$  2Fe + 3CO  
ZnO + C  $\xrightarrow{\Delta}$  Zn + CO  
SnO<sub>2</sub> + 2C  $\xrightarrow{\Delta}$  Sn + 2CO  
CuO + C  $\xrightarrow{\Delta}$  Cu + CO

In case of zinc, which is volatile at the temperature at which reduction is being carried out, reduction cannot be done in open furnace.

Reduction by using carbon cannot be done in the cases where the free metal formed has tendency to form carbide, i.e. metal has more affinity for carbon as compared to oxygen.

Carbon monoxide as reducing agent: In some cases, CO produced in the furnace itself acts as reducing agent.

$$Fe_{3}O_{4} + 4CO \xrightarrow{\Delta} 3Fe + 4CO_{2}$$

$$Fe_{2}O_{3} + 3CO \xrightarrow{\Delta} 2Fe + 3CO_{2}$$

$$PbO + CO \xrightarrow{\Delta} Pb + CO_{2}$$

$$CuO + CO \xrightarrow{\Delta} Cu + CO_{2}$$

**Production of iron from the oxide ore:** The extraction of iron, the most important industrial metal, is carried out in a blast furnace. The charge consists of iron ores (haematite  $\operatorname{Fe_2O_3}$  and magnetite  $\operatorname{Fe_3O_4}$ ), coke and limestone, which is heated with a blast of air. As the exothermic reaction proceeds, a composition and temperature gradient is set up in the furnace. Below 1123 K, CO reduces the ores to FeC. Reduction to Fe by CO can occur at about 1123 K and that direct reduction, in which the reducing agent is C, can occur at about 1123 K. In this region, limestone also decomposes to CaO and  $\operatorname{CO_2}$  and slag formation takes place.

**Note:** Apart from the integrated steel plants that produce steel out of pig iron from blast furnaces, steel is also produced by electronic arc furnaces and induction furnace units using steel scrap, sponge iron as feed material. While integrated steel plants produce mainly mild steel in bulk quantities, the electronic steel-making units produce mild steel as well as alloy steel, including stainless steel.

**Hydrogen as reducing agent:** Hydrogen gas (H<sub>2</sub>) is difficult to use because of its inflammable nature.

$$WO_3 + 3H_2 \xrightarrow{\Delta} W + 3H_2O$$
  
 $MoO_3 + 3H_2 \xrightarrow{\Delta} Mo + 3H_2O$   
 $GeO_2 + 2H_2 \xrightarrow{\Delta} Ge + 2H_2O$ 

**Aluminium as reducing agent:** Aluminium powder is used to reduce metallic oxides to metal. The process is known as aluminothermic process or Goldschmidt thermic process. It is a strong exothermic reaction.

Metallic oxides such as TiO<sub>2</sub>, Cr<sub>2</sub>O<sub>3</sub>, and Mn<sub>3</sub>O<sub>4</sub> are reduced to Ti, Cr, and Mn, respectively.

$$3\text{TiO}_2 + 4\text{Al} \longrightarrow 2\text{Al}_2\text{O}_3 + 3\text{Ti}$$
 $\text{Cr}_2\text{O}_3 + 2\text{Al} \longrightarrow \text{Al}_2\text{O}_3 + 2\text{Cr}$ 
 $3\text{Mn}_3\text{O}_4 + 8\text{Al} \longrightarrow 4\text{Al}_2\text{O}_3 + 9\text{Mn}$ 

Magnesium as reducing agent:

$$Rb_2O_3 + 3Mg \longrightarrow 3MgO + 2Rb$$
 $TiCl_4 + 2Mg \xrightarrow{\Delta} Ti + 2MgCl_2$  (Kroll's process)

### 1.4.6.2 Auto-reduction or Self-reduction Process

In certain cases, no reducing agent is required. The sulphides of less electropositive metals such as mercury (Hg), copper (Cu), lead (Pb), tin (Sn) are reduced without the use of any additional reducing agent.

When the ores are heated in air, a part of these ores is changed into the oxide or sulphate, which then reacts with the remaining part of the ore, to give the metal and SO<sub>2</sub> as shown below:

1. Extraction of mercury from cinnabar (HgS)

$$2HgS + 3O_2 \longrightarrow 2HgO + 2SO_2$$
  
Cinnabar

$$2HgO + HgS \longrightarrow 3Hg + 3SO_2$$

2. Extraction of copper from copper glance (Cu<sub>2</sub>S)

$$\begin{array}{c} 2\mathrm{Cu_2S} + 3\mathrm{O_2} \longrightarrow 2\mathrm{Cu_2O} + 2\mathrm{SO_2} \\ \mathrm{Copper} \\ \mathrm{glance} \end{array}$$

$$2Cu_2O + Cu_2S \longrightarrow 6Cu + SO_2$$

Copper (Cu) so obtained is known as **blister copper** because as it solidifies, SO<sub>2</sub> hidden in it escapes out producing blisters on the surface.

3. Extraction of lead from galena (PbS)

$$2PbS + 3O_2 \longrightarrow 2PbO + 2SO_2$$
Galena

$$2PbO + PbS \longrightarrow 3Pb + SO_2$$

or 
$$PbS + 2O_2 \longrightarrow PbSO_4$$
  
 $PbSO_4 + PbS \longrightarrow 2Pb + 2SO_2$ 

Elevated temperature and the anion/s associated with the metal may bring about this change.

All roasting/smelting processes mentioned above make use of reverberatory furnaces at some stage. Oil burners shoot along intensely hot flame down the furnace and melt the charges. On the walls there are suitable tap holes for crude metals and the slag. Such a furnace may melt upto 106 kg of charge per day. Smelting operations can also be carried out in converters. Air is blown through the molten material, when the impurities are largely removed as volatile oxidation products. Also magnesite linings are used in converters to slag off any metallic impurities, Converters may be of two types:

- Bessemer converter, similar to that used in metallurgy of iron.
- 2. Peirce-Smith converter, which consists of a large horizontal steel drum resting upon rollers. Rolls of steel tubes (tuyeres) pass into the converter and are connected to an air duct. Air is forced into the molten bath of crude metal. The process provides its own heat due to the oxidation of impurities and the temperature rises to ~2673 K.

# 1.4.6.3 Electrolytic Reduction Method

When the chemical reduction method is not applicable, electrolytic reduction is done. Electrolytic reduction is of two types:

- 1. Reduction at high temperature in the absence of water, molten electrolyte is used.
- Electrolysis at low temperature using water hydrometallurgy. Cost factor is low.

Reduction at high temperature is mainly used for alkali and alkaline earth metals Zn and Al. Their oxides are very stable and hence in order to reduce their oxides to free metal, they have to be heated at a very high temperature with carbon. But at a high temperature, these metals react with carbon to form carbides. Thus, such metals cannot be extracted by reducing their oxides with carbon. These are, however, extracted by electrolysis of their oxides, hydroxides or chlorides in fused state. The metal is liberated at the cathode. Some other salt has to be added to lower down the melting point of the compound taken. For example,

Extraction of Na by the electrolysis of fused mixture of NaCl and CaCl<sub>2</sub> by Down Process. [For details, refer "Inorganic Chemistry for Joint Entrance Examination JEE (Advanced) Part 1" by K. S. Verma Chapter 4, Section 4.9.1]. Various reactions taking place in the electrolytic cell are as follows:

**Fusion:** NaCl  $\Longrightarrow$  Na $^{\oplus}$  + Cl $^{\bigcirc}$ 

**Electrolysis:** 

At cathode: Reduction  $Na^{\oplus} + e^{\Theta} \longrightarrow Na$ 

At anode: Oxidation  $Cl^{\Theta} \longrightarrow Cl + e^{\Theta}$ 

 $Cl + Cl \longrightarrow Cl_2 \uparrow$ 

Hence at cathode, Na metal is discharged, whereas at anode,  $Cl_2$  gas is discharged. The products react rapidly and hence suitable arrangements are made to keep them separate.  $CaCl_2$  is added in the above process as:

- a. It lowers down the melting point of NaCl.
- b. Discharge potential of Ca<sup>2+</sup> is much higher than Na<sup>⊕</sup>, hence Na<sup>⊕</sup> is discharged.
- 2. Extraction of Al: AlCl<sub>3</sub> is not chosen; rather, Al<sub>2</sub>O<sub>3</sub> is chosen, since AlCl<sub>3</sub> is a covalent compound and does not conduct electricity. Al<sub>2</sub>O<sub>3</sub> is a high melting compound and hence cryolite, (Na<sub>3</sub>AlF<sub>6</sub>) is added to it. It dissolves Al<sub>2</sub>O<sub>3</sub>. This dissolution is easily done at 700–1000°C. Graphite electrodes are used for the removal of Al.

# 1.4.6.4 Aluminium Metal Extraction from Bauxite

Aluminium metal is extracted from bauxite in a two-stage process. In the first stage, pure alumina  $(Al_2O_3)$  is obtained from bauxite and in the second stage, electrolysis of  $Al_2O_3$  in molten cryolite  $(Na_3AlF_6)$  is carried out to obtain aluminium metal.

Bauxite contains SiO<sub>2</sub>, iron oxides and titanium (IV) oxide as impurities. The bauxite ore is digested with a concentrated solution of sodium hydroxide at 473-523 K and 35-36 bar pressure. Aluminium oxide and silica dissolve to form sodium aluminate and sodium silicate respectively leaving behind iron oxide and TiO<sub>2</sub> which are filtered off.

$$\mathrm{Al_2O_3(s)} + 2\mathrm{NaOH(aq)} + 3\mathrm{H_2O}(\mathit{l}) \rightarrow 2\mathrm{Na[Al(OH)_4](aq)}$$

The filterate containing sodium aluminate and sodium silicate is diluted and seeded with freshly precipitated aluminium hydroxide which induces the precipitation of aluminium hydroxide leaving behind sodium silicate in solution.

$$Na[Al(OH)_{4}(aq) \xrightarrow{\ \ H_{2}O\ \ } Al(OH)_{3}(s) + NaOH(aq)$$

The aluminium hydroxide is filtered, dried and calcined at 1473 K to yield pure alumina. Aluminium is obtained from alumina by electrolysis; this is known as **Hall-Heroult process**. The modern electrolysis process uses synthetic cryolite, Na<sub>3</sub>AlF<sub>6</sub>. Typical electrolyte composition ranges are Na<sub>3</sub>AlF<sub>6</sub>(80-85%), CaF<sub>2</sub>(5-7%), AlF<sub>3</sub>(5-7%), Al<sub>2</sub>O<sub>3</sub>(2-8%) intermittently recharged. The electrolysis of this mixture is carried out in an electrolytic cell (schematically shown in figure) using carbon electrodes. The oxygen liberated at the anode reacts with the carbon anode producing CO and CO<sub>2</sub>. The overall reactions may be written as:

Cathode:  $Al^{3+}$  (melt)  $+ 3e^{-} \rightarrow Al(l)$ 

Anode:  $C(s) + O^{2-} (melt) \rightarrow CO(g) + 2e^{-}$ ,

$$C(s) + 2O^{2-}$$
 (melt)  $\rightarrow CO_2(g) + 4e^{-}$ 

- a. The electrode potential in aqueous system as given in emf series for the reduction of metal ions differs from the potential needed for the deposition of metal in molten state.
- b. Electrode potential in aqueous system is largely influenced by hydration enthalpies, whereas in molten state, these are absent.
- c. In molten state, ions are in direct influence with each other, and there is no hydration sphere.
- d. In both the cases, ionisation enthalpies are of great significance.

**e.** Decomposition potential in molten state is temperature dependent.

**Discharge potential**, i.e., the potential at which a metal is discharged at cathode depends on:

- a. Position of metal in electrochemical series: Lower the  $E^{\Theta}$  value, lower is the discharge potential.
- **b.** Concentration of the metal ions in the electrolyte: Greater the concentration, lower is the discharge potential.

#### ILLUSTRATION 1.3

- a. Metal sulphides occur mainly in rocks and metal halides occur in lakes and seas. Give reason.
- b. Pine oil is used in froth flotation process. Why?
- c. What is a depressant? Give an example.
- d. What is the role of stabiliser in froth flotation process?
- e. What is gangue?

#### Sol.

- a. Metal halides being soluble in water get dissolved in rain water and are carried to lakes and seas during weathering of rocks. On the other hand, metal sulphides being insoluble are left behind in the rocks as residue.
- b. Pine oil increases the non-wetability of ore particles by water, i.e., ore particles are preferentially wetted by pine oil and hence become lighter and rise to the surface along with the froth.
- **c.** Depressants are compounds which prevent the formation of froth in froth flotation process. For example, NaCN acts as a depressant for ZnS in the separation of ZnS ore from PbS ore.
- **d.** Chemical compounds namely aniline and cresols, which tend to stabilise the froth in froth flotation process, are called froth stabilisers.
- **e.** The earthy and siliceous impurities associated with ores is called gangue.

# ILLUSTRATION 1.4

- 1. Metals occur in the native form because of their
  - a. High electronegativity
- b. Low reactivity
- c. Low density
- d. High reactivity
- 2. Specific gravity of slag is
  - a. Higher than molten metal
  - b. Same as that of molten metal
  - c. Less as that of molten metal
  - d. None of the above
- 3. Which process is used for the extraction of metals from their sulphide ores?
  - a. Smelting

- b. Froth flotation
- c. Electrolysis
- d. Metal displacement
- 4. Calamine is an ore of
  - a. Hg

b. Zn

c. Ca

- d. Cd
- 5. Non-fusible impurities of ores are removed by adding
  - a. Slag

b. Flux

c. Gangue

d. None

### 1.12 Inorganic Chemistry

- **6.** Common method of extraction of metals from oxide ore involves
  - a. Reduction with aluminium b. Reduction with carbon
  - c. Reduction with hydrogen d. Electrolytic method
- 7. Smelting is the reduction of oxide to metal by
  - a. Carbon
- b. Hydrogen
- c. Aluminium
- d. Electric current
- 8. During froth flotation process, commonly used frother is
  - a. CuSO<sub>4</sub>
- b. NaCN + alkali
- c. Pine oil
- d. Potassium xanthate
- 9. Iron ores are dressed by
  - a. Froth flotation process
- b. Hand picking
- c. Magnetic separation
- d. All of the above
- 10. Silicon is the main constituent of
  - a. Alloys
- b. Rocks
- c. Animals
- d. Plants

- Sol. 1. b
- 2. b
- **3.** b
- 4. b 5. b

- 6. b
- 7. a
- **8.** c
- **9.** c
- **10.** b

# CONCEPT APPLICATION EXERCISE 1.1

- 1. Why is Fe an abundant element on earth, and why are the elements with higher atomic number increasingly rare?
- 2. Name the chief forms of the occurrence of the following in the earth's crust:
  - a. Aluminium
- b. Calcium
- c. Sodium
- d. Lead
- 3. Outline the principles of refining of metals by the following methods:
  - a. Electrolytic refining
- **b.** Zone refining
- c. Vapour phase refining
- **4.** Predict the modes of occurrence of the following three types of metals:
  - a. Highly reactive (e.g. Na)
  - **b.** Moderately reactive (e.g. Fe)
  - c. Noble metal (e.g. Au)
- 5. Why metal ores are not found as their nitrates?
- **6.** During the reduction of TiCl<sub>4</sub> by magnesium why helium not nitrogen is preferred?
- 7. Write the name and chemical formula of an ore of tungsten which contains tungestate ion.
- **8.** (i) Name the process used in the manufacture of steel from spiegel and (ii) the alloy of spiegel.
- **9.** Hydrometallurgy, pyrometallurgy and electrometallurgy are used for the extraction of which metals.
- **10.** Name the process and metal used in large scale extraction of Cr and Mn.
- 11. Why a sulphide ore of copper is heated in a furnace after mixing with flux?
- 12. How wrought iron is obtained from cast iron?
- 13. How the impurities of S, Si, and P are removed from cast iron?
- 14. How ZnS and PbS are separated by froth flotation process?

# 1.5 THERMODYNAMICS OF METALLURGY

The basic concept of thermodynamics is useful in the following ways:

- 1. Selecting the element which will be the most suitable reducing agent for a particular oxide during a metallurgical operation.
- 2. Predicting the optimum temperature at which the reduction can occur smoothly.

For any reaction or process, Gibb's free energy change  $(\Delta G)_{is}$  given by the equation

$$\Delta G = \Delta H - T \Delta S \qquad \dots (i)$$

where

 $\Delta H$  = enthalpy change,

 $\Delta S$  = entropy change and

T = absolute temperature.

The free energy change is also related to the equilibrium constant, K of the reaction at temperature T by the following equation

$$\Delta G = -RT \ln K \qquad ... (ii)$$

For any reaction to be feasible at any temperature,  $\Delta G$  must be negative. In Eq. (i), if  $\Delta G$  is – ve, K will be +ve. This means that the reaction will proceed to form the products. One can conclude the following:

- 1. Greater the -ve value of  $\Delta G$ , more spontaneous is the reaction.  $\Delta G$  will be negative when
  - **a.**  $\Delta H = -\text{ve}$  and  $T\Delta S = +\text{ve}$  (At any temperature)
  - **b.**  $\Delta H = -\text{ve}$  and  $T\Delta S = -\text{ve}$  (Temperature should be low)
  - c.  $\Delta H = +ve$  and  $T\Delta S = +ve$

 $(T\Delta S > \Delta H \text{ and temperature should be high})$ 

2. A reaction with +ve value of  $\Delta G$  can still be made to occur if it is coupled with another reaction having a high -ve value of  $\Delta G$ , so that the net  $\Delta G$  of both the reactions is -ve. Above-mentioned coupling reaction can be easily understood using Ellingham diagram.

# 1.5.1 ELLINGHAM DIAGRAM

Ellingham diagram usually consists of plots of  $\Delta_{\mathcal{G}}^{\odot}$  vs T for the formation of oxides of various elements. Similar diagrams can also be drawn for sulphides and halides of various elements. These diagrams can be used to predict the feasibility of thermal reduction of an ore. For example, consider the formation of metal oxide  $(M_{\mathcal{G}}O)$ .

$$2xM_{(s)} + O_{2(g)} \longrightarrow 2M_xO_{(s)}$$

In this reaction,  $O_2$ , a gas, is used up and  $M_xO_{(s)}$ , a solid formed. Since gases have higher entropy than solids,  $\Delta S$  become negative. Thus, on increasing the temperature,  $T\Delta_x S^{\odot}$  become more negative.

In the equation  $\Delta_f G^{\odot} = \Delta_f H^{\odot} - T \Delta_f S$ ;  $T \Delta S$  is subtracted, hence  $\Delta_f G^{\odot}$  becomes less and less negative, i.e.,  $\Delta_f G^{\odot}$  increases with increase in temperature. In other words, lines in  $\Delta_f G^{\odot}$  vs T plothave +ve slopes for most of the reactions involving the formation of metal oxides. The following observations are made from the  $\Delta_f G^{\odot}$  vs T diagram (Figure 1.6).

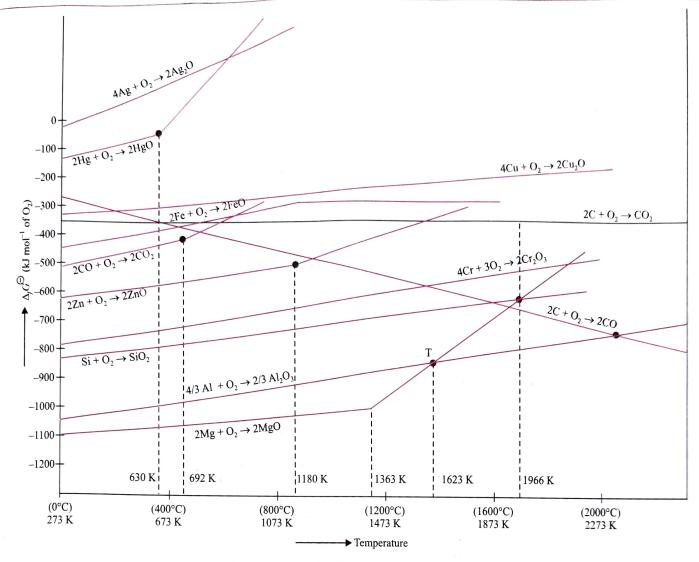


Fig. 1.6 Elingham diagram for formation of oxides of some elements

- 1. The slope of the curves of the formation of metal oxides is +ve as  $\Delta_f G^{\ominus}$  becomes less negative or increases with rise in temperature.
- 2. Each plot is a straight line except when some change in phase, i.e., solid → liquid or liquid → gas takes place. The temperature at which such a change occurs is indicated by an increase in the slope on the +ve side. For example, in the Zn–ZnO plot, there is an abrupt increase in +ve slope at 692 K and 1180 K, which indicates the phase change from Zn<sub>(s)</sub> → Zn<sub>(l)</sub>, Zn<sub>(l)</sub> → Zn<sub>(g)</sub>. Thus 692 K is the melting point and 1180 K is the boiling point of zinc metal.
- 3. In case of less reactive metals such as Ag and Hg,  $\Delta_f G^{\odot}$  has more +ve value at high temperatures. This implies that both Ag<sub>2</sub>O and HgO are unstable and decompose at high temperatures.

$$2Ag_2O \xrightarrow{\Delta} 4Ag + O_2$$
$$2HgO \xrightarrow{\Delta} 2Hg + O_2$$

- 4. In the plot of CO,  $\Delta_f G^{\odot}$  decreases as  $\Delta_f S^{\odot}$  increases, this is indicated by downward trend.
- 5. Any metal oxide with lower value of  $\Delta_f G^{\ominus}$  is more stable as compared to metal oxide with higher value of  $\Delta_f G^{\ominus}$ .

Hence, the metal oxide placed higher in the plot can be reduced by the metal involved in the formation of oxide placed lower in the diagram. For example,

**a.** Cr<sub>2</sub>O<sub>3</sub> can be reduced by Al metal, but Al<sub>2</sub>O<sub>3</sub> cannot be reduced by Cr.

$$Cr_2O_3 + 2Al \longrightarrow Cr + Al_2O_3$$

**b.** ZnO can be reduced by Si, but SiO<sub>2</sub> cannot be reduced by Zn.

$$2ZnO + Si \longrightarrow SiO_2 + 2Zn$$

The relative tendency of various elements to act as reducing agent is

#### 1.5.2 LIMITATIONS OF ELLINGHAM DIAGRAM

Ellingham diagram simply predicts whether the reduction of a particular oxide with a specific reducing agent is possible or not. Limitations of Ellingham diagram are as follows:

 Kinetics of reduction: It does not tell anything about the kinetics of the reduction reaction, i.e., whether the reduction reaction is slow or fast. 2. Reactant/product equilibrium: The interpretation of  $\Delta_t G^{\oplus}$  is based on the equilibrium constant K.

$$\Delta_f G^{\bigodot} = RT \ln K.$$

Thus, it is assumed that reactants and products are in equilibrium.

$$M_{\nu}O + A \Longrightarrow xM + AO$$

But this is not always true as the reactant/product may be solid.

# 1.5.3 REDUCING NATURE OF CARBON

The process of extracting a metal by reduction of its oxide with carbon (in form of coke, charcoal or carbon monoxide) is called

Carbon (graphite) is used as reducing agent, and it forms two different types of oxides, i.e., CO and CO2. The stability of these oxides varies with the temperature. Three different reactions are possible, which are as follows:

1. 
$$C_{(s)} + O_{2(g)} \longrightarrow CO_{2(g)}$$
 ... (i)  
 $S^{\Theta}(JK^{-1}mol^{-1})$  5.5 205 214  
at 298 K

$$\Delta_{f} S^{\Theta} = [214 - (205 + 5.5)] = -3.5 \text{ JK}^{-1} \text{mol}^{-1}$$
**2.** 
$$2C_{(s)} + O_{2(g)} \longrightarrow 2CO_{(g)} \qquad \dots \text{ (ii)}$$

$$S^{\Theta} (\text{JK}^{-1} \text{mol}^{-1}) \quad 5.5 \quad 205 \quad 198$$

at 298 K

$$\Delta_{f} S^{\Theta} = [2 \times 198 - (2 \times 5.5 + 205)] = 180 \text{ JK}^{-1} \text{mol}^{-1}$$

$$2\text{CO}_{(g)} + \text{O}_{2(g)} \longrightarrow 2\text{CO}_{2(g)} \quad \dots \text{(iii)}$$

$$S^{\Theta} (\text{JK}^{-1} \text{mol}^{-1}) \quad 198 \quad 205 \quad 214$$

at 298 K

$$\Delta_f S^{\Theta} = [2 \times 214 - (2 \times 198 + 205)] = -173 \text{ JK}^{-1} \text{mol}^{-1}$$

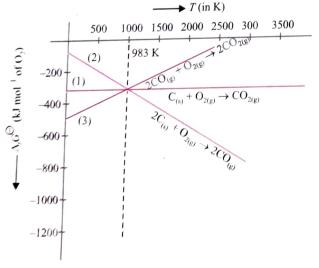


Fig. 1.7 Ellingham diagram for the reducing nature of carbon

- From line (1), it is concluded that C combines with O<sub>2</sub> at all temperatures forming  ${\rm CO_2}$  and with the increase in temperature, there is hardly any change in  $\Delta_r G^{\odot}$  value.
- From line (2), it is concluded that as the temperature increases,  $\Delta G^{\odot}$  becomes more and more negative. Likelihood of the reaction to occur increases with temperature.

- From line (3), it is concluded that with the increase in temperature,  $\Delta_j G^{\odot}$  becomes more and more positive and hence likelihood of the reaction to occur decreases, i.e. Co becomes more stable than CO<sub>2</sub>.
- At 983 K, i.e. the temperature at which the three lines intersect,  $\Delta_i G^{\circ}$  for the forward reaction is equal to  $\Delta_i G^{\circ}$ for the backward reaction or  $\Delta_f G^{\odot}$  for the reaction is  $z_{ero}$

$$\Delta_t G^{\odot} = -2.303 \ RT \log K = 0$$

where K = equilibrium constant

$$\log K = 0 \text{ or } K = 1$$

- Below 983 K,  $\Delta_{i}G^{\Theta}(CO_{2})$  is more negative than  $\Delta_{i}G^{\Theta}(CO_{1})$ and hence CO<sub>2</sub> will be formed predominantly. It is further concluded that below 983 K, CO acts as a better reducing agent than C.
- Above 983 K,  $\Delta G^{\Theta}(CO)$  is more negative than  $\Delta G^{\Theta}(CO)$ and hence CO will be formed predominantly.

Reduction with C at high temperatures is not preferred in all cases due to the following reasons:

- 1. High cost factor i.e. it is uneconomical.
- 2. Few metals react with C at high temperatures and form carbides.
- 3. Practical difficulties in maintenance of high temperature.

# 1.5.4 THEORY OF REDUCTION OF METAL OXIDE WITH CARBON

During reduction, the decomposition of the metal oxide takes place **Reduction:**  $M_r O_{(s)} \longrightarrow x M_{(s \text{ or } l)} + 1/2 O_{2(g)}$ and the reducing agent takes away the oxygen given by the metal oxide.

Oxidation: 
$$C_{(s)} + 1/2O_{2(g)} \longrightarrow CO_{(g)}$$
 ... (ii

In this case, the role of the reducing agent is to provide a large negative  $\Delta_{f}G^{\Theta}$  to make the sum of  $\Delta_{f}G^{\Theta}$  values of the above two reactions (i.e., reduction of the metal oxide and oxidation of the reducing agent) negative.

Reversing Eq. (i) one gets equation representing the oxidation of the metal.

$$xM_{(s \text{ or } l)} + 1/2 \text{ O}_{2(g)} \longrightarrow M_xO_{(s)}; \ \Delta_j G^{\Theta}_{(M, M_xO)} \qquad \dots (iii)$$

However, instead of partial oxidation of C to CO, if complete oxidation of C to CO<sub>2</sub> occurs, the oxidation of the reducing agent may be represented as follows:

$$\frac{1}{2} C_{(s)} + \frac{1}{2} O_{2(g)} \longrightarrow \frac{1}{2} CO_{2(g)}; \ \frac{1}{2} \Delta_j G^{\Theta}_{(C, CO_2)} \qquad \dots (iv)$$

If, instead of C, CO is used as the reducing agent, the oxidation of the reducing agent may be represented as follows:

$$CO_{(g)} + \frac{1}{2} O_{2(g)} \longrightarrow \frac{1}{2} CO_{2(g)}; \ \Delta_j G^{\Theta}_{(CO, CO_2)} \qquad \dots (v)$$

On subtracting Eq. (iii) from each of the three Eq. (ii), (iv), and (v), we have

$$M_x O_{(s)} + C_{(s)} \longrightarrow x M_{(s \text{ or } l)} + CO_{(g)}$$
 ... (vi)

$$M_x O_{(s)} + \frac{1}{2} C_{(s)} \longrightarrow x M_{(s \text{ or } l)} + \frac{1}{2} CO_{2(g)}$$
 ...  $(v^{[j]})$ 

$$M_{vO_{(g)}} + CO_{(g)} \longrightarrow xM_{(g \text{ or } I)} + CO_{(g)}$$
 ... (viii)

Equations (vi), (vii) and (viii) describe the actual reduction of the metal oxide  $M_xO$  to the free metal M. The  $\Delta_yG^{\odot}$  values for these reactions, in general, can be obtained, by subtraction of the corresponding  $\Delta_yG^{\odot}$  values from the Ellingham diagram. If these values are –ve, the reduction is feasible, otherwise not.

Alternatively, without going into the calculations for  $\Delta_f G^{\odot}$ feasibility of a reduction process can be predicted simply by looking at the Ellingham diagram. Metals for which free energy of formation  $(\Delta_r G^{\odot})$  of their oxides is more negative can reduce those metals for which the free energy of formation  $(\Delta, G^{\odot})$  of their respective oxides is less negative. In other words, at any given temperature, any element. (metal) will reduce the oxide of other metals which lie above it in the Ellingham diagram because the free energy change  $(\Delta_t G^{\odot})$  for the combined redox reaction will be negative by an amount equal to the difference between the free energy of formation  $(\Delta_r G^{\odot})$  of the two oxides at that temperature. Further, greater the difference, easier is the reduction. For example, Mg can reduce Al<sub>2</sub>O<sub>3</sub>, ZnO, FeO and Cu<sub>2</sub>O more readily than Al can reduce ZnO, FeO and Cu<sub>2</sub>O. Similarly, Al can reduce ZnO, FeO and Cu2O more readily than Zn reduces FeO and Cu<sub>2</sub>O. Thus, the relative tendency of these metals to act as reducing agents is Mg > Al > Zn > Fe > Cu.

However in case of less reactive metals such as silver and mercury  $\Delta_f G^{\odot}$  becomes positive at higher temperatures. This suggests that both silver oxide (Ag<sub>2</sub>O) and mercury oxide (HgO) are unstable and hence decompose at high temperatures to liberate the corresponding metal.

$$2\mathrm{Ag_2O_{(s)}} \xrightarrow{\mathrm{Heat}} 4\mathrm{Ag_{(s)}} + \mathrm{O_{2(g)}}; 2\mathrm{HgO_{(s)}} \xrightarrow{630\;\mathrm{K}} 2\mathrm{Hg_{(l)}} + \mathrm{O_{2(g)}}$$

# 1.5.5 EFFECT OF TEMPERATURE ON △, G° OF THE OVERALL REDUCTION PROCESS

For any process,  $\Delta G = \Delta H - T\Delta S$ . On increasing the temperature, the values of  $\Delta H$  and  $\Delta S$  nearly remain constant, hence the value of  $\Delta_f G^{\odot}$  becomes more negative. This implies that if a particular reduction process does not occur at a lower temperature, it may occur at a higher temperature. What is required is to select the temperature in such a way that the  $\Delta_f G^{\odot}$  value of the overall redox reaction becomes negative.

In the Ellingham diagram, this temperature is indicated by the intersection of the two curves, i.e., curve for formation of  $M_xO$  and the curve for the oxidation of the reducing agent. At the point of intersection of the two curves,  $\Delta_f G^{\odot} = 0$ . Below this temperature,  $\Delta_f G^{\odot}$  is -ve and hence the oxide is stable. Above this temperature,  $\Delta_f G^{\odot}$  is +ve and hence the oxide is unstable, i.e., it would give metal and oxygen. For example, the temperature at the intersection point T of the (Al, Al<sub>2</sub>O<sub>3</sub>) and (Mg, MgO) curves is approximately 1623 K. Therefore, below 1623 K, MgO is stable and Mg can reduce Al<sub>2</sub>O<sub>3</sub> to Al.

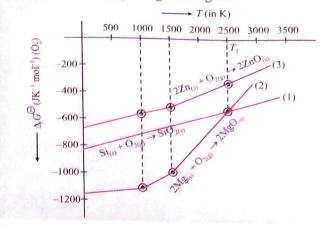
$$Al_2O_{3(s)} + 3Mg_{(s)} \longrightarrow 3MgO_{(s)} + 2Al_{(s)}$$

But above 1623 K,  $Al_2O_3$  is more stable and hence Al can reduce MgO to Mg.

$$3MgO_{(s)} + 2Al_{(s)} \longrightarrow Al_2O_{3(s)} + 3Mg_{(s)}$$

# ILLUSTRATION 1.5

Interpret the following Ellingham diagram.



### Sol.

1.  $Si_{(s)} + O_{2(g)} \longrightarrow 2SiO_{2(s)}$ As temperature increases  $\Lambda G^{\ominus}$  becomes

As temperature increases,  $\Delta_f G^{\odot}$  becomes less negative, hence  $SiO_{2(s)}$  becomes less stable, i.e., at 500 K,  $SiO_2$  is more stable than 2500 K.

2. 
$$2Mg_{(s)} + O_{2(g)} \longrightarrow 2MgO_{(s)}$$

Abrupt changes in the plot at  $\sim\!800~\rm K$  and  $\sim\!1400~\rm K$  denote phase change/transition from s  $\longrightarrow$  l and l  $\longrightarrow$  g, respectively and represent melting point ( $\sim\!800~\rm K$ ) and boiling point ( $\sim\!1400~\rm K$ ). MgO<sub>(s)</sub> becomes less stable with increase in temperature.

At  $T_1$ , lines of (1) and (2) intersect. One can conclude the following:

- **a.** At  $T_1$ , both MgO and SiO<sub>2</sub> are equally stable.
- **b.** At temperature  $> T_1$ , MgO is less stable than SiO<sub>2</sub>. Hence, Si will reduce MgO to Mg.

$$2MgO + Si \longrightarrow SiO_2 + 2Mg$$

c. At temperature  $< T_1$ , SiO<sub>2</sub> is less stable than MgO. Hence, Mg will reduce SiO<sub>2</sub> to Si.

$$SiO_2 + 2Mg \longrightarrow 2MgO + Si$$

Relative stability of MgO and SiO<sub>2</sub> at given temperature can be predicted with the help of Ellingham diagram.

3. 
$$2Zn_{(s)} + O_{2(g)} \longrightarrow 2ZnO_{(s)}$$
  
 $\Delta_f G^{\Theta}(ZnO) > \Delta_f G^{\Theta}(MgO)$   
 $\Delta_f G^{\Theta}(ZnO) > \Delta_f G^{\Theta}(SiO_5)$ 

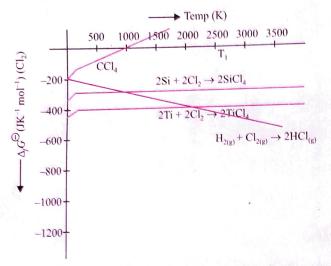
Hence, both  $Mg_{(s)}$  and  $Si_{(s)}$  can be used as reducing agent for reducing  $ZnO_{(s)}$  to  $Zn_{(s)}$ .

# **Important Points:**

- Element to be used as reducing agent must form stable oxide than the metal oxide to be reduced.
- 2. The more negative the  $\Delta_f G^{\odot}$  value for oxide formation at a given temperature, the more difficult it is to reduce the metal oxide concerned.

3. When the plot for one metal is below that for another, the first metal is thermodynamically capable of reducing the oxide of the second.

# Reduction of chlorides by C:



The reaction that should take place when C is used for reducing chlorides is

$$\begin{split} & 4\mathrm{MCl}_{(\mathrm{s})} + \mathrm{C}_{(\mathrm{s})} \longrightarrow 4\mathrm{M}_{(\mathrm{s})} + \mathrm{CCl}_{4(\mathrm{g})} \\ & \Delta_f G^{\bigodot}\left(\mathrm{CCl}_4,\,\mathrm{g}\right) < \Delta_f G^{\bigodot}\left(\mathrm{MCl},\,\mathrm{s}\right) \end{split}$$

Carbon cannot be used as reducing agent to reduce chlorides because  $\Delta_f G^{\odot}(CCl_4)$  is less negative than  $Cl_2$ .  $H_2$  can be used above a certain temperature if it is not forming interstitial hydride.

# 1.5.6 APPLICATION OF ELLINGHAM DIAGRAM IN PYROMETALLURGY

The utility of Ellingham diagrams in pyrometallurgy can be illustrated by considering in detail the extraction of iron, copper, and zinc from their respective oxides.

### 1.5.6.1 Extraction of Iron from Its Oxides

The chief ores of iron are as follow:

S.No.	S.No. Ore Formula	
1.	Haematite	Fe <sub>2</sub> O <sub>3</sub> (red oxide of iron)
2.	Magnetite	Fe <sub>3</sub> O <sub>4</sub> (magnetic ore of iron)
3.	Limonite	Fe <sub>2</sub> O <sub>3</sub> ·3H <sub>2</sub> O (hydrated ore of iron)
4.	Iron pyrites	Fe <sub>2</sub> S (also known as fool's gold)
5.	Siderite	FeCO <sub>3</sub> (or spathic ore)

### Different forms of iron:

- 1. Cast iron or pig iron: Impure form and contains 2.5-4% of carbon along with impurities of S, Si, P, and Mn. It is brittle, resistant to corrosion, and is used for sewage pipes.
- 2. Wrought iron or malleable iron: Purest form and contains minimum amount of carbon (0.12–0.25%), malleable, can be welded, structurally weak, cannot be magnetised, used for making wires, chains, electromagnets, etc.
- 3. Steel: It contains 0.2–1.5% of carbon; steels containing 0.2–0.5% of C are known as mild steels, while those containing 0.5–1.5% carbon are called hard steel.

**Heat treatment of steel:** The hardness of steel can be controlled by heat treatment as discussed below:

- Quenching: Process of heating steel to redness and then sudden cooling by plunging in water or oil. The steel obtained is hard and brittle.
- 2. Annealing: Process of heating steel to redness and then cooling slowly. Steel obtained is soft.
- **3. Tempering:** Process of heating the quenched steel to a temperature much below redness (200–350°C) and then cooling slowly. Used in making razor blades, axes, knives, swords, etc.
- **4. Case-hardening:** Process of heating wrought iron or mild steel in contact with charcoal and then quenching in oil.
- 5. Nitriding: Process of heating steels at about 700°C in an atmosphere of ammonia. It gives a hard coating of iron nitride on the surface of steel.

For extraction of iron from its oxide ore, usually **haematite** is used. Process of extraction involves the following steps:

- Concentration: The ore is crushed in jaw crushers. Crushed ore is concentrated by gravity separation process in which the crushed ore is washed in a stream of water, when lighter sand and clay particles are washed away, while the heavier ore particles settle down. In case of sulphide ore (iron pyrites), concentration is carried out by froth flotation process.
- 2. Calcination: The concentrated ore is then calcined, i.e., heated strongly in the presence of a limited supply of air in a reverberatory furnace. Following changes are observed:
  - a. Moisture is removed.
  - **b.** Impurities of sulphur, phosphorus, and arsenic escape as their volatile oxides.

$$S_8 + 8O_2 \longrightarrow 8SO_2 \uparrow; P_4 + 5O_2 \longrightarrow P_4O_{10} \uparrow;$$
  
 $2As + 5O_2 \longrightarrow As_2O_5 \uparrow$ 

c. Ferrous oxide is oxidised to ferric oxide, thereby preventing the loss of iron as slag during smelting.

$$4\text{FeO}_{(s)} + \text{O}_{2(g)} \longrightarrow 2\text{Fe}_2\text{O}_{3(s)}$$

**d.** The ore becomes porous and hence is more suitable for reduction to the metallic state. In case of carbonate ore (siderite), during calcination it is converted into ferrous oxide.

$$FeCO_{3(s)} \longrightarrow FeO_{(s)} + CO_{2(g)}$$

$$4FeO_{(s)} + O_{2(g)} \longrightarrow 2Fe_2O_{3(s)}$$

However, in case of sulphide ore (iron pyrites), conversion to oxide is carried out by roasting.

$$4\text{FeS}_{2(s)} + 11\text{O}_{2(g)} \longrightarrow 2\text{Fe}_2\text{O}_{3(s)} + 8\text{SO}_{2(g)}$$

3. Smelting: The calcined ore is reduced with carbon i.e. smelted in a blast furnace (Figure 1.8). Blast furnace is a tall cylindrical furnace made of steel and lined inside with fire bricks. It is slightly narrow at the top and again at the bottom. This facilitates the proper flow of materials. The furnace is provided with a double cup and cone arrangement, which helps to feed the charge from the top without letting any gases from inside to escape. Near the top, furnace is

also provided with an outlet for waste gases. At the base, the furnace is provided with

- Small pipes called tuyeres through which a blast of hot air is admitted.
- **b.** A tapping hole for withdrawing molten iron.
- **c.** A slag hole for withdrawing slag.

The charge consisting of calcined ore (8 parts), coke (4 parts), and limestone (1 part) is introduced into the furnace from the top through cup and cone arrangement. At the same time, a blast of hot air pre-heated to about 1000 K is blown into the furnace through tuyeres. The added coke serves both as a fuel as well as a reducing agent, while added limestone acts as the basic flux.

The temperature near the top of the furnace is  $\sim$ 523 K while near the bottom it is  $\sim$ 2170 K.

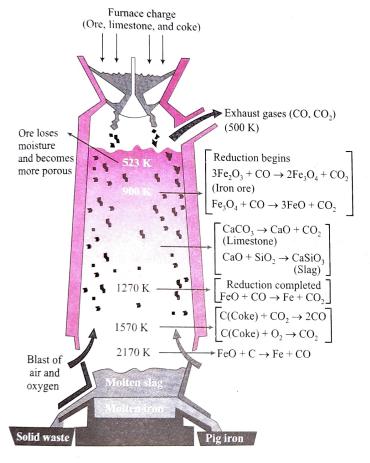


Fig. 1.8 Blast furnace

**a.** Theory of reduction process: Iron oxide is reduced to iron mainly by CO, though perhaps some reduction by C also takes place.

$$FeO_{(s)} + C_{(s)} \longrightarrow Fe_{(s/I)} + CO_{(g)}$$
 ... (i)

This redox reaction can be divided into the following two half reaction:

#### i. Reduction:

$$\operatorname{FeO}_{(s)} \longrightarrow + \operatorname{Fe}_{(s)} + \frac{1}{2} \operatorname{O}_{2(g)}; \Delta_f G^{\ominus}_{(\operatorname{FeO}, \operatorname{Fe})} \qquad \dots \text{ (ii)}$$

#### ii. Oxidation:

$$C_{(s)} + \frac{1}{2} O_{2(g)} \longrightarrow CO_{(g)}; \Delta G^{\Theta}_{(C, CO)}$$
 ... (iii)

The net free energy change of these two combined reactions is

$$\Delta_{f}G_{(C,CO)}^{\Theta} + \Delta_{f}G_{(FeO,Fe)}^{\Theta} = \Delta_{f}G^{\Theta}$$
 ... (iv)

The resultant reaction, i.e., Eq. (i), will take place only when  $\Delta_i G^{\Theta}$  is -ve.

To find the approximate temperature at which this reduction occurs, consider the Ellingham diagram (Figure 1.9).

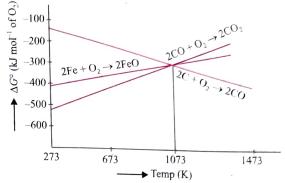


Fig. 1.9 Ellingham diagram for formation of FeO from Fe, CO from C and CO, from CO

At approximately 1073 K or above, the (C, CO) line is much below the (Fe, FeO) line. This means,  $\Delta_f G^{\ominus}_{Fe, FeO} > \Delta_f G^{\ominus}_{C, CO}$  and hence  $\Delta_f G^{\ominus}_{is}$  is -ve.

In other words, at 1073 K or above, coke will reduce FeO to Fe and itself will be oxidised to CO.

In contrast, at temperature 1073 K, the (CO, CO<sub>2</sub>) line lies below (Fe, FeO) line. Therefore, below 1073 K, CO reduces the oxides of iron, i.e., Fe<sub>2</sub>O<sub>3</sub>, Fe<sub>3</sub>O<sub>4</sub>, etc.

Thus, in the blast furnace, reduction of iron oxides takes place at different temperatures. Since the air passes through in a few seconds, the individual reactions do not reach equilibrium.

#### b. Reactions occuring in the furnace

 Zone of combustion: Near the tuyeres, coke burns to form carbon dioxide.

$$C_{(s)} + O_{2(s)} \longrightarrow CO_{2(g)}; \Delta_f H^{\odot} = -393.3 \text{ kJ}$$

As the reaction is exothermic, lot of heat is produced and the temperature is  $\sim$ 2170 K.

ii. Zone of heat absorption: It is the lower part of the furnace and the temperature lies between 1423 and 1673 K. As CO<sub>2</sub> formed near tuyeres moves up, it meets the descending charge. The coke present in the charge reduces CO<sub>2</sub> to CO.

$$CO_{2(g)} + C_{(g)} \longrightarrow 2CO_{(g)}; \Delta H = +163.2 \text{ kJ}$$

Since this reaction is endothermic, the temperature gradually changes to 1423 K.

iii. Zone of slag formation: It is the middle part of the furnace and the temperature is around 1123 K.

In this zone, limestone decomposes to form CaO and CO<sub>2</sub>. The CaO thus formed acts as a flux and combines with silica (present as an impurity) to form fusible calcium silicate slag.

$$CaCO_{3(s)} \xrightarrow{-1123 \text{ K}} CaO_{(s)} + CO_{2(g)}$$

$$CaO_{(s)} + SiO_{2(s)} \xrightarrow{-1123 \text{ K}} CaSiO_{3(s)}$$
Calcium silicate (slag)

**iv. Zone of reduction:** It is the upper part of the furnace. The temperature is between 500–900 K. In this zone, the ores are reduced to FeO by CO.

$$\begin{split} &3\mathrm{Fe_2O_{3(s)}} + \mathrm{CO_{(g)}} \xrightarrow{573-673 \text{ K}} 2\mathrm{Fe_3O_{4(s)}} + \mathrm{CO_{2(g)}} \\ &\mathrm{Fe_3O_{4(s)}} + \mathrm{CO_{(g)}} \xrightarrow{773-873 \text{ K}} 3\mathrm{FeO_{(s)}} + \mathrm{CO_{2(g)}} \\ &\mathrm{Fe_2O_{3(s)}} + \mathrm{CO_{(g)}} \xrightarrow{773-873 \text{ K}} 2\mathrm{FeO_{(s)}} + \mathrm{CO_{2(g)}} \end{split}$$

But the further reduction of FeO to Fe by CO occurs around 1123 K.

$$FeO_{(s)} + CO(g) \xrightarrow{-1123 \text{ K}} Fe_{(s)} + CO_{2(g)}$$

However, direct reduction of iron ores (i.e., haematite magnetite etc), left unreduced around 873 K, occurs completely to iron by carbon above 1123 K.

$$Fe_2O_{3(s)} + 3C_{(s)} \xrightarrow{> 1123 \text{ K}} 2Fe_{(s/l)} + 3CO_{(g)}$$

v. Zone of fusion: This is the lower part of the furnace. Temperature here lies between 1423 and 1673 K. In this region, spongy iron melts and dissolves some C, S\*, P\*, Si\*, Mn, etc. CaSiO<sub>3</sub> slag also melts in this region. Both the molten slag and the molten iron trickle down into hearth, where they form two separate layers. The molten CaSiO<sub>3</sub> slag being lighter forms the upper layer, while molten iron being heavier forms the lower layer. The two liquids are periodically tapped off. The iron thus obtained from the furnace contains about 4% carbon and many impurities (e.g., S, P, Si, Mn) in smaller amount. This is called pig iron and is cast into variety of shapes. Cast iron is different from pig iron and is made by melting pig iron with scrap iron and coke using hot air blast. It has slightly lower carbon content (about 3%) and is extremely hard and brittle.

**Note:** S\*, P\* and Si\* are produced from sulphates, phosphates and silicates, respectively, present in the ore by reduction with carbon.

# 1.5.6.2 Wrought Iron

Wrought iron is the purest form of commercial iron. It contains about 0.2–0.5% carbon besides traces of P and Si in the form of slag. Carbon in wrought iron is present partly as graphite and partly as cementite (Fe<sub>3</sub>C). Wrought iron is ductile, soft and malleable. The presence of slag in it makes it tough and resistant towards rusting and corrosion. It is, therefore, used to make chains, anchors, bolts, nails and railway carriage couplings. It can be easily magnetised and hence is used to make magnets in electric cranes and dynamos.

1. Preparation: Wrought iron is prepared from cast iron by decreasing the carbon content and oxidising the impurities (S, P, Si, Mn, etc.) in a reverberatory furnace lined inside with haematite. The haematite oxidises C to CO, S to SO<sub>2</sub>, Si to SiO<sub>2</sub>, P to P<sub>4</sub>O<sub>10</sub> and Mn to MnO.

$$Fe_2O_{3(s)} + 3C_{(s)} \longrightarrow 2Fe_{(s)} + 3CO_{(g)}$$

$$2\operatorname{Fe}_{2}\operatorname{O}_{3(s)} + 3\operatorname{S}_{(s)} \longrightarrow 4\operatorname{Fe}_{(s)} + 3\operatorname{SO}_{2(g)}$$

$$2\operatorname{Fe}_{2}\operatorname{O}_{3(s)} + 3\operatorname{Si}_{(s)} \longrightarrow 4\operatorname{Fe}_{(s)} + 3\operatorname{SiO}_{2(g)}$$

$$10\operatorname{Fe}_{2}\operatorname{O}_{3(s)} + 3\operatorname{P}_{4(s)} \longrightarrow 20\operatorname{Fe}_{(s)} + 3\operatorname{P}_{4}\operatorname{O}_{10(s)}$$

$$\operatorname{Fe}_{2}\operatorname{O}_{3(s)} + 3\operatorname{Mn}_{(s)} \longrightarrow 2\operatorname{Fe}_{(s)} + 3\operatorname{MnO}_{(s)}$$

$$\operatorname{Fe}_{2}\operatorname{O}_{3(s)} + 3\operatorname{Mn}_{(s)} \longrightarrow 2\operatorname{Fe}_{(s)} + 3\operatorname{MnO}_{(s)}$$

CO and  $SO_2$  thus escape, whereas manganous oxide (MnO) and silica (SiO<sub>2</sub>) combine to form slag.

$$\mathsf{MnO}_{(s)} + \mathsf{SiO}_{2(s)} {\longrightarrow} \mathsf{MnSiO}_{3(l)}$$

Manganous silicate (slag)

Similarly, phosphorus pentoxide combines with haematite to form ferric phosphate slag:

$$2\text{Fe}_2\text{O}_{3(s)} + \text{P}_4\text{O}_{10(g)} \longrightarrow 4\text{FePO}_{4(l)}$$

Ferric phosphate (slag)

Sometimes, limestone is added as a flux, which helps to remove SiO<sub>2</sub> as CaSiO<sub>3</sub> slag. After the reduction, the metal is removed from the furnace and is freed from the slag by passing through rollers.

# 2. Properties of cast iron:

- a. It is extremely tough and melts at 1500°C and is highly malleable and ductile.
- **b.** Due to presence of 1% slag, it is fibrous and hence can withstand high stresses.
- **c.** It softens at about 1000°C, and then it can be forged and welded.
- **d.** It can be tempered and magnetised, as it has high magnetic permeability.

# 3. Use of wrought iron:

- **a.** It is used for articles capable of standing high stresses, such as chains, nails, hooks, bolts, etc.
- b. It is used for making bars and wires.
- c. It is used for electromagnets and agriculture equipment.

# 1.5.6.3 Manufacture of Steel

It can be prepared by any of the following processes:

- 1. Bessemer process
- 2. Open hearth process
- 3. LD process
- 1. Bessemer process: This process involves the use of a large egg-or pear-shaped vessel called Bessemer converter. This is made of steel plates lined with silica (SiO<sub>2</sub>) or magnesia (MgO) depending upon the nature of impurities present in cast iron. If the impurities are acidic, such as P<sub>4</sub>O<sub>10</sub> or SO<sub>2</sub> basic lining or lime (CaO) or magnesia (MgO) is used, known as 'basic process'. If impurities are basic such as MnO, lining of silica (SiO<sub>2</sub>) bricks is used, known as 'acidic process'. In operation, hot air blast is passed through the molten pig iron. Silicon and manganese (in acidic process) or phosphorous (in basic process) are oxidised to their oxides and are removed as slag.

#### Acidic process:

$$Si + O_2 \longrightarrow SiO_2$$
  
 $2Mn + O_2 \longrightarrow 2MnO$ 

$$MnO + SiO_2 \longrightarrow MnSiO_3$$
 (slag)

### Basic process:

$$P_4 + SO_2 \longrightarrow P_4O_{10}$$
  
 $P_4O_{10} \longrightarrow 2Ca_3(PO_4)_2$  (Thomas slag)

Finally oxidation of carbon takes places forming CO, which burns with a blue flame at the mouth of the converter. When no more CO is produced (i.e., flame disappears), a calculated amount of Spiegeleisen (an alloy of Fe, Mn and C) is added and distributed throughout the mass by blowing air some time. Mn and C serve as de-oxidiser and reduce FeO (if any) as the rest dissolves in molten steel. (Mn makes steel harder and increases its tensile strength.)

- 2. Open hearth process: It is a modern process based on the following principles:
  - **a.** Impurities present in cast iron are oxidised by adding iron ores.
  - **b.** Percentage of C and Si is brought down by adding scrap iron or low grade wrought iron.
  - **c.** High temperature is maintained by regenerated system of heat economy.

The charge consisting of cast iron, scrap iron, and haematite is melted in an open hearth furnace. It is lined with lime of magnesia bricks (basic process) for P and S and silica bricks (acidic process) for C, Si, Mn. The furnace is heated by preheated producer gas  $(CO + N_2) + a$  little  $CO_2$  and work on regenerated system.

# Acidic process:

$$\begin{aligned} &2\mathrm{Fe_2O} + 3\mathrm{Si} \longrightarrow 4\mathrm{Fe} + 3\mathrm{SiO_2} \\ &\mathrm{Fe_2O_3} + 3\mathrm{Mn} \longrightarrow 2\mathrm{Fe} + 3\mathrm{MnO} \\ &\mathrm{MnO} + \mathrm{SiO_2} \longrightarrow \mathrm{MnSiO_3} \, (\mathrm{slag}) \end{aligned}$$

#### **Basic process:**

$$10\text{Fe}_2\text{O} + 12\text{P} \longrightarrow 20\text{Fe} + 3\text{P}_4\text{O}_{10}$$

$$P_4\text{O}_{10} + 6\text{CaO} \longrightarrow 2\text{Ca}_3(\text{PO}_4)_2 \text{ (slag)}$$

$$\text{SiO}_2 + \text{CaO} \longrightarrow \text{CaSiO}_3$$

$$\text{SiO}_2 + \text{MnO} \longrightarrow \text{MnSiO}_3 \text{ (slag)}$$

Finally C and S are oxidised forming volatile gases.

$$Fe_2O_3 + 3C \longrightarrow 2Fe + 3CO \uparrow$$
  
 $2Fe_2O_3 + 3S \longrightarrow 4Fe + 3SO_2 \uparrow$ 

Samples of steel are drawn from time to time and tested for their carbon contents. At the appropriate time, ferromanganese or spiegeleisen is added to the molten mass to obtain mild or hard steel, respectively. This process takes 8–10 hr for completion (while Bessemer process takes only 20–30 min). While the molten steel is drawn from the furnace, a little aluminium or ferrosilicon is added to it to remove dissolved gases.

3. LD process: In this process, pure oxygen under a pressure of about 6 to 10 atm is blown through a water-cooled copper tube (called lance) from a distance of 24 inches over the surface of molten cast iron containing up to 18% scarp iron and taken in a converter with basic lining. Impurities of

Si, Mn, P and C are oxidised rapidly and form a slag. The purified metal has a higher density and sinks to the bottom, while its place is taken by impure metal. Thus, convection currents are set up in the converter and the conversion of cast iron into steel is completed in about 45 min. The oxidation reaction being exothermic keeps the whole mass in molten condition.

**Properties and uses of steel:** Steel combines the use of cast iron and wrought iron. It is hard and elastic. The properties of steel depend upon its carbon content. As percentage C increases, hardness increases but ductility decreases.

- Low carbon or soft steel contains 0.25% C.
- Medium carbon or mild steel contains 0–0.5% C.
- High carbon or hard steel contains 0.5–1.5% C.
- Alloy steel or special steels are alloys of steel with Ni, Cr, Co, Mn, V, W etc.

## Alloys of steel:

Alloy	Composition	Properties	Uses
Alnico	Fe-60%, Ni-20%, Al-12%, Co-8%	Highly magnetic	For making per- manent magnets
Chrome steel	Cr-2-4%	High tensile strength	For making ax- les, ball bearing, and cutting tools
Invar	Ni-36%	Low coefficient of expansion	For making watches, metre scales, and pen- dulum rods
Manganese steel	Mn-13%	Very hard and resistant to wear and tear	For making rock drills, safes, etc.
Nickel steel	Ni-2-4%	Resistant to corrosion, hard and elastic	For making wire cables, gears, and shafts
Stainless steel	Cr-18%, Ni-8%, C-1%	Resists corrosion	For making utensils, cutlery, and ornamental pieces
Tungsten steel	W-5%, C-1%	Retains hard- ness at high temperature	For making high speed cutting tools

# 1.5.6.4 Extraction of Copper from Cuprous Oxide [Copper(I) Oxide]

In the Ellingham diagram given in figure 1.10, (Cu, Cu<sub>2</sub>O) curve is almost at the top, while the (C, CO) and (CO, CO<sub>2</sub>) lines lie much below it particularly in the temperature range  $500-600\,\mathrm{K}$ . This means that it is very easy to reduce cuprous oxide to metallic copper by heating with coke. But most of the ores of copper are sulphides. Hence, the sulphide ores are first roasted in a reverberatory furnace to convert them into oxides.

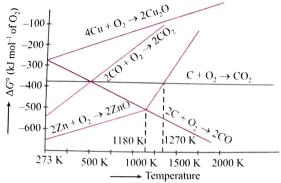


Fig. 1.10 Ellingham diagram showing the formation of Cu<sub>2</sub>O from Cu, ZnO from Zn, CO from C, and CO<sub>2</sub> from C and CO

$$2Cu_2S + 3O_2 \longrightarrow 2Cu_2O + 2SO_2$$

The oxides can then be reduced to metallic copper using coke as the reducing agent.

$$Cu_2O + C \longrightarrow 2Cu + CO$$

However, in actual process, the sulphide ore (i.e. copper pyrites), after concentration by froth flotation process is roasted in a reverberatory furnace when copper pyrites is converted into a mixtue of FeS and Cu<sub>2</sub>S, which, in turn, are partially oxidised.

$$2\text{CuFeS}_2 + \text{O}_2 \longrightarrow \text{Cu}_2\text{S} + 2\text{FeS} + \text{SO}_2$$
  
Copper pyrites  
 $2\text{FeS} + 3\text{O}_2 \longrightarrow 2\text{FeO} + 2\text{SO}_2$   
 $2\text{Cu}_2\text{S} + 3\text{O}_2 \longrightarrow 2\text{Cu}_2\text{O} + 2\text{SO}_2$ 

Since iron is more reactive than copper, FeS is preferentially oxidised to FeO than Cu<sub>2</sub>S to Cu<sub>2</sub>O. If at all any Cu<sub>2</sub>O is formed, it combines with FeS and is changed back to Cu<sub>2</sub>S.

$$Cu_2O + FeS \longrightarrow Cu_2S + FeO$$

Thus, the roasted ore mainly contains Cu<sub>2</sub>S and FeO along with some unreacted FeS.

The roasted ore is then mixed with silica (flux) and some powdered coke (to check the oxidation of FeO to  $Fe_2O_3$ ) and heated strongly in a blast furnace. This process is called smelting.

During smelting, FeO combines with silica to form fusible ferrous silicate slag.

$$FeO + SiO_2 \longrightarrow FeSiO_3$$
Silica

At the temperature of the furnace, the entire mass melts and two layers of molten mass are formed. The slag being lighter makes the upper layer, which can be withdrawn from the slag hole from time to time. The lower molten layer is called **copper matte**. It chiefly consists of Cu<sub>2</sub>S and some unchanged FeS.

Recovery of copper from matte: The molten matte is transferred to a Bessemer converter, which is a pear-shaped furnace made of steel and lined inside with silica. It is mounted on a horizontal axel and can be tilted in any position. It is fitted with small pipes called tuyeres through which a blast of hot air and fine sand is admitted.

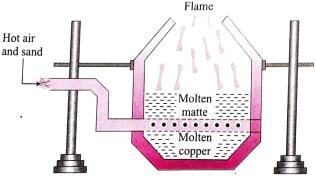


FIg. 1.11 Bessemer converter

During the process of Bessemerisation, any sulphur, arsenic and antimony still present as impurity in matte escape as their respective volatile oxides while FeS is oxidised to FeO, which combines with silica to form FeSiO<sub>3</sub> slag.

$$2FeS + 3O_2 \longrightarrow 2FeO + 2SO_2$$
  
 $FeO + SiO_2 \longrightarrow FeSiO_3(slag)$ 

The slag thus formed melts and floats on the top of the molten mass and is removed. When whole of iron has been removed  $a_{S}$  slag, some of the cuprous sulphide undergoes oxidation to form cuprous oxide, which then reacts with cuprous sulphide to form copper metal.

$$2Cu_2S + 3O_2 \longrightarrow Cu_2O + 2SO_2$$
  
 $2Cu_2O + Cu_2S \longrightarrow 6Cu + SO_2$ 

Copper metal so produced falls below tuyeres and thus escapes the oxidising action of the blast. After the completion of the reaction, the converter is tilted and the molten metal is poured in sand moulds. As the metal cools, dissolved SO<sub>2</sub> escapes. Some of the gas bubbles are, however, entrapped during solidification giving blister-like appearance to the metal. The impure metal (containing about 1% impurity) thus obtained is, therefore, called blister copper. Blister copper is finally purified by electrolytic refining as discussed in previous section.

#### 1.5.6.5 Extraction of Zinc from Zinc Oxide

From Ellingham diagram, it is evident that intersection of the ( $Z_{IL}$ ,  $Z_{IL}$ ,  $Z_{IL}$ ) and (C, CO) curves lies at a higher temperature than that of the ( $C_{IL}$ ,  $C_{IL}$ ) and (C and CO) curves. Therefore, reduction of  $Z_{IL}$ 0 with coke is carried out at a higher temperature than that of  $C_{IL}$ 0.

Further, all the three curves representing the oxidation of carbon [i.e., (C, CO), (C, CO<sub>2</sub>) and (CO, CO<sub>2</sub>)] lie above the oxidation curve of Zn till the boiling point of zinc (i.e., 1180 K) is reached. Therefore, above 1180 K,  $\Delta_f G^{\odot}$  for the formation of CO decreases while that for the formation of ZnO increases very rapidly and intersects the (C, CO<sub>2</sub>) curve at 1270 K.

In other words, above 170 K,  $\Delta_{I}G^{\odot}$  for ZnO is higher than that of CO<sub>2</sub> and CO from carbon. Therefore, above 1270 K  $\Delta_{I}G^{\odot}$  for the reduction of ZnO by carbon is negative and hence ZnO is easily reduced by coke above 1270 K. For the purpose of reduction, ZnO is made into briquettes with coke and clay and heated above 1270 K usually around 1673 K, so that the reduction process essentially goes to completion.

It may, however, be noted here that  $\Delta_j G^{\odot}$  of  $CO_2$  from  $CO_3$  always higher than that of ZnO. Therefore, CO cannot be used for reduction of ZnO to Zn.

Since the boiling point of zinc is low (1180 K), the metal is distilled off and collected by rapid chilling.

# ILLUSTRATION 1.6

- a. Suggest a condition under which magnesium could reduce alumina.
- b. Although thermodynamically feasible, in practice magnesium metal is not used for the reduction of aluming in the metallurgy of aluminium. Why?
- c. Why is the reduction of a metal oxide easier if the metal formed is in liquid state at the temperature of reduction?

# Sol.

a. The two equations are:

i. 
$$\frac{4}{3}$$
 Al + O<sub>2</sub>  $\longrightarrow \frac{2}{3}$  Al<sub>2</sub>O<sub>3</sub>

ii. 
$$2Mg + O_2 \longrightarrow 2MgO$$

All the point of intersection of the  $Al_2O_3$  and MgO curves,  $\Delta_rG^{\Theta}$  becomes zero for the reaction:

$$\frac{2}{3} \text{Al}_2 \text{O}_3 + 2 \text{Mg} \longrightarrow 2 \text{MgO} + \frac{4}{3} \text{Al}$$

Below that point magnesium can reduce alumina.

- b. Temperatures below the point of intersection of Al<sub>2</sub>O<sub>3</sub> and MgO curves, magnesium can reduce alumina. But the process will be uneconomical as magnesium is much costlier than alumina.
- c. The entropy is higher if the metal is in liquid state than when it is in solid state. The value of entropy change  $(\Delta_r G^{\Theta})$  of the reduction process is more on positive side when the metal formed is in liquid state and the metal oxide being reduced is in solid state. Thus, the value of  $\Delta_r G^{\Theta}$  becomes more on negative side and the reduction becomes easier.
- d. Zinc being above iron in the electrochemical series (more reactive metal is zinc), the reduction will be faster in case zinc scraps are used. But zinc is costlier metal than iron, so using iron scraps will be advisable and advantageous.

# ILLUSTRATION 1.7

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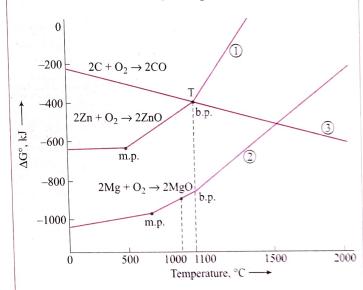
Why is it advantageous to roast a sulphide ore to the oxide before reduction?

**Sol.** The free energies of formation  $(\Delta_1 G^{\Theta})$  of most sulphides are greater than those for  $CS_2$  and  $H_2S$ . Carbon disulphide is, in fact, an endothermic compound. So neither carbon nor hydrogen is a suitable reducing agent for metal sulphides. Moreover, the roasting of a sulphide to the oxide is quite advantageous thermodynamically. Hence, the common practice is to roast sulphide ore to the oxide prior to reduction.

# CONCEPT APPLICATION EXERCISE 1.2

- 1. What is the thermodynamic consideration in the choice of a reducing agent in metallurgy?
- 2. Carbon monoxide is more effective reducing agent than carbon below 983 K but above this temperature, the reverse is true. How would you explain this?
- 3. The choice of a reducing agent in a particular case depends on thermodynamic factor. How far do you agree with this statement? Support your opinion with example.

- 4. Which is a better reducing agent at 710°C: C or CO?
  - **5.** Indicate the temperature at which carbon can be used as a reducing agent for FeO.
  - **6.** Is it true that under certain conditions, Mg can reduce SiO<sub>2</sub>, and Si can reduce MgO?
  - 7. Which methods would you recommend for the purification of impure metals such as zinc, copper and germanium metals?
  - 8. Explain by Ellingham diagram?
    - (a) At temperature above 1073 K, coke can be used to reduce FeO to Fe.
    - (b) CO is more effective reducing agent than C, below 983 K but above this temperature, the reverse is true.
    - (c) Which basic concept is involved in selecting a reducing agent for obtaining metal from its oxide ore?
  - **9.** The Ellingham diagram for zinc, magnesium and carbon converting into corresponding oxides is shown below:



(a) What should be the temperature to make the following reduction process spontaneous.

$$ZnO + C \longrightarrow Zn + CO$$

- (b) At what temperature Zn and C have equal affinity for O<sub>2</sub>?
- (c) At 1100°C which reaction is spontaneous to a maximum extent.

(i) 
$$MgO + C \longrightarrow Mg + CO$$

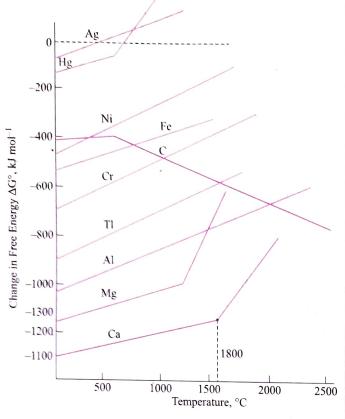
(ii) 
$$ZnO + C \longrightarrow Zn + CO$$

(iii) MgO + Zn
$$\longrightarrow$$
 Mg + ZnO

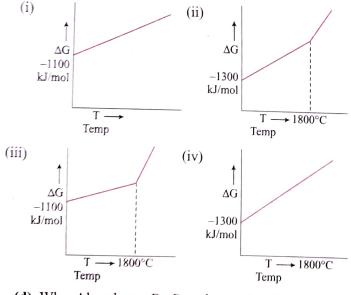
(iv) 
$$ZnO + Mg \longrightarrow MgO + Zn$$

**10.** Using the following Ellingham diagram answer the following questions:

Thorganic Chemistry



- (a) Free energy change of Mg and Hg for the conversion to oxides, the slope  $\Delta G$  vs. T, changes above the boiling of the given metal. Explain.
- (b) Out of Hg, Mg, Fe and Al, which element can be prepared by heating the oxide above 400°C.
- (c) For the conversion of Ca(s) to CaO(s) which of the following represents the  $\Delta G$  vs. T?



(d) Why Al reduces Fe<sub>2</sub>O<sub>3</sub> whereas MgO cannot be reduced by Al at 1500°C. Explain.

# .6 ELECTROCHEMICAL PRINCIPLES OF METALLURGY

s discussed in section 1.5, the principles of thermodynamics e useful in:

1. Selecting a suitable reducing agent for a given metal oxide.

2. Selecting optimum temperature at which reduction reaction proceeds smoothly.

Same principles can also be applied in the reduction of metal ions in solution or molten state. These reductions are usually carried out either by electrolysis or by adding a suitable element as the reducing agent.

The process of electrolysis has been used to carry out the reduction of molten metal salts. The electrochemical principles of electrolysis can be understood through equation:

$$\Delta G^{\Theta} = -nFE^{\Theta} \qquad ... (i)$$

where n is the number of electrons involved in the reduction process,  $E^{\Theta}$  is the standard electrode potential of the redox couple  $(M/M^{n+})$  present in the system. More reactive metals have large negative values of electrode potentials and hence are difficult to reduce. If the difference in  $E^{\Theta}$  values of two redox couples is positive, and consequently  $\Delta G^{\Theta}$  in Eq. (i) is negative, then the more reactive metal will displace the less reactive metal from the solution. In other words, less reactive metal will come out of the solution and the more reactive metal will go into the solution. For example,

$$\begin{array}{ccc} Cu^{2^{+}}_{\phantom{2}(aq)} + & Fe_{(s)} & \longrightarrow Cu_{(s)} + Fe^{2^{+}}_{\phantom{2}(aq)} \\ & \text{More} & \text{Less} \\ & \text{reactive} & \text{reactive} \\ & \text{metal} & \text{metal} \end{array}$$

In simple electrolysis, the ions are discharged at the cathode (negative electrode) and deposited there.

$$M^{n+}_{(aq)} + ne^{\Theta} \longrightarrow M_{(s)}$$

Depending upon the reactivity of the metal produced, the materials of the electrodes are selected. Sometimes, a flux is added for making the molten mass more conducting.

# 1.6.1 APPLICATIONS OF ELECTROLYSIS TO METALLURGY

The process of extraction of metals by electrolysis of their fused salts is called electrometallurgy. In this process, electrons serve as the reducing agent.

1. Extraction of copper from low grade ores and scraps: Copper is extracted by hydrometallurgy from low grade ores. The low grade ores are leached by treating with an acid of bacteria when copper metal goes into solution as Cu<sup>2+</sup> ions. The solution containing Cu<sup>2+</sup> ions is then treated with scrap iron or H<sub>2</sub> gas.

$$Cu^{2+}_{(aq)} + Fe_{(s)} \longrightarrow Cu_{(s)} + Fe^{2+}_{(aq)}$$

$$Cu^{2+}_{(aq)} + H_{2(g)} \longrightarrow Cu_{(s)} + 2H^{\oplus}_{(aq)}$$

Since  $E^{\Theta}$  of Fe<sup>2+</sup>/Fe (-0.44 V) or that of H<sup> $\oplus$ </sup>/H<sub>2</sub> (0.0 V) redox couple is lower than that of Cu<sup>2+</sup>/Cu (+0.34 V), Fe or H<sub>2</sub> can displace Cu from Cu<sup>2+</sup> ions.

2. Extraction of aluminium from alumina: Fused alumina (Al<sub>2</sub>O<sub>3</sub>) is a bad conductor of electricity. Therefore, cryolite (Na<sub>3</sub>AlF<sub>6</sub>) and fluorspar (CaF<sub>2</sub>) are added to purified alumina, which not only make alumina a good conductor of electricity but also reduce the melting point of the mix to around 1140 K.

The process of obtaining aluminium by electrolysis of a mixture of purified alumina and cryolite is called Hall and Heroult process.

The electrolysis of the molten mass is carried out in an electrolytic cell or tank (Figure 1.12) made of iron using carbon electrodes. The molten electrolyte is covered with a layer of powdered coke to prevent oxidation and loss of heat due to radiation. The temperature of the bath is maintained around 1173 K.

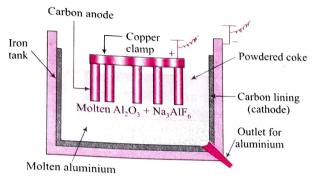


Fig. 1.12 Electrolytic cell for the extraction of aluminium

The reactions taking place during the electrolysis are as follows:

Cathode: 
$$Al^{3+}_{(melt)} + 3e^{\Theta} \longrightarrow Al_{(l)}$$
  
Anode:  $C(s) + O^{2-}_{(melt)} \longrightarrow CO_{(g)} + 2e^{\Theta}$   
 $C(s) + 2O^{2-}_{(melt)} \longrightarrow CO_{2(g)} + 4e^{\Theta}$ 

The aluminium metal liberated at the cathode melts at the high temperature (1173 K) of the tank. The molten metal being heavier than the molten electrolyte sinks to the bottom of the tank from where it is withdrawn periodically through the tapping hole. The metal obtained by this process is about 99.95% pure.

# 1.7 EXTRACTION OF METALS BY BOTH **OXIDATION AND REDUCTION**

Extraction of gold and silver: We have already discussed in Section 1.4.4.4 that extraction of gold and silver involves leaching of the metals present in the ore with  $CN^{\Theta}$  ions. This is also an oxidation reaction because during the leaching process, Ag is oxidised to  $Ag^{\oplus}$  and Au to  $Au^{\oplus}$ , which then combine with  $CN^{\ominus}$ ions to form their respective soluble complexes.

fons to form their respective solutions to form their respective solutions to form their respective solutions 
$$4Ag_{(s)} + 8CN^{\ominus}_{(aq)} + 2H_2O_{(l)} + O_{2(g)}$$
Silver
$$\longrightarrow 4[Ag(CN)_2]^{\ominus}_{(aq)} + 4OH^{\ominus}_{(aq)}$$
Soluble complex
$$4Au_{(s)} + 8CN^{\ominus}_{(aq)} + 2H_2O_{(1)} + O_{2(g)}$$
Gold
$$\longrightarrow 4[Au(CN)_2]^{\ominus}_{(aq)} + 4OH^{\ominus}_{(aq)}$$

The metals are then recovered from these complexes by reduction or displacement method using a more electropositive zinc metal.

inc metal. 
$$2[\mathrm{Ag(CN)_2}]^{\ominus}_{(aq)} + \mathrm{Zn_{(s)}} \longrightarrow 2\mathrm{Ag_{(s)}} + [\mathrm{Zn(CN)_4}]^{2-}_{(aq)}$$
 
$$2[\mathrm{Au(CN)_2}]_{(aq)} + \mathrm{Zn_{(s)}} \longrightarrow 2\mathrm{Au(s)} + [\mathrm{Zn(CN)_4}]^{2-}_{(aq)}$$
 In these displacement reactions, zinc acts as the reducing agent.

Like extraction of copper from low grade copper ores, gold and silver are also extracted from these ores by hydrometallurgy. The process of extraction of metals by dissolving the ore in a suitable reagent followed by precipitation or displacement of the metal by a more reactive or more electropositive metal is called

# 1.8 REFINING OR PURIFICATION **OF METALS**

Refining or purification of metals is still required as the metal obtained by any of the processes/methods discussed in the previous sections still has certain impurities present in it and is thus known as crude metal.

To obtain metal of high purity, various refining techniques methods are employed depending upon the nature of metal and impurities. Some refining processes are as follows:

- 1. Distillation
- 2. Liquation
- 3. Zone refining
- 4. Electrolysis
- 5. Vapour phase refining

These refining processes are discussed in detail in the following sections:

# 1.8.1 DISTILLATION

Distillation is used for purification of low boiling point or volatile metals, such as mercury (Hg), zinc (Zn), cadmium (Cd) etc. The pure metal is heated and its vapours are separately condensed in a receiver. While the pure metal distils out, impurities (non-volatile) are left behind.

### 1.8.2 LIQUATION

Liquation is used to concentrate as well as purify metals such as bismuth, tin, lead, mercury, etc, whose melting points are lower than that of the impurities or when the impurity is less fusible than the metal itself.

Impure metal in the form of blocks (ingots) is placed on the sloping hearth (usually of reverberatory furnace). On being heated to a temperature slightly greater than the melting point of pure metal, the metal flows down the hearth, while the impurities (infusible material) are left behind on the hearth (Figure 1.13) charge (impure metal).

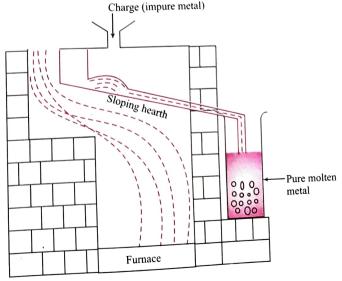


Fig. 1.13 Liquation

# 1.8.3 ZONE REFINING (FRACTIONAL CRYSTALLISATION)

Zone refining is based on the principle that impurities are more soluble in the melt that in the pure metal (solid). It is used for the purification of germanium, silicon, gallium etc. Metals of high purity can be obtained by removing the impurity, which shows different solubility in the solid and liquid states of the metal. When impure molten metal begins to solidify, the pure metal crystallises, while impurities remain in the melt (liquid).

Impure metal is cast in the form of a rod. This metal rod is enclosed in a tube of inert material. A circular mobile heater is fixed at one end of the rod (enclosed in inert material covering). This whole set-up is enclosed in an inert atmosphere to prevent oxidation of the metal (Figure 1.14). As the heater is moved slowly along the length of the rod, pure metal crystallises out of the melt, whereas the impurities remain suspended in the melt. As the heater is moved, the impurities move along with the heater and get collected at the other end of the rod.

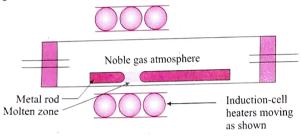


Fig. 1.14 Zone refining

The process is repeated a number of times until the desired state of purity is reached. The end of the rod, where the impurities get collected, is finally chopped off. This method is specially useful for producing semiconductors of very high purity; for example, silicon, germanium purified by this method contain as little as 7–10 ppm of impurities.

#### 1.8.4 ELECTROLYSIS OR ELECTROLYTIC REFINING

Metals such as Cu, Ag, Zn, Sn, Pb, Cr, etc., are refined by electrolysing aqueous solution of their appropriate salts or a complex of the metal (electrolyte). The blocks of impure metal forms the anode, while thin sheet of pure metal acts as cathode. The cathode and anode are suspended in the electrolyte. On passing electric current, at a suitable voltage, metal ions from electrolyte are deposited on the cathode in the form of pure metal, while an equivalent amount of metal dissolves from the anode and goes into the electrolyte solution as metal ions.

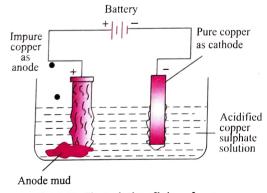


Fig. 1.15 Electrolytic refining of copper

Electrolytic refining results in the transfer of pure metal from the anode to the cathode. The voltage applied for electrolysis is such that the impurities of more electropositive metals remain in

the solution as ions, whereas impurities of the less electropositive metals settles under the anode as anode mud or anode sludge.

For example, in case of Cu refining by electrolysis (Figure 1.15) cathode is the block of impure Cu metal or blister copper, and anode is the thin sheet of pure copper. Electrolyte is copper sulphate solution acidified with sulphuric acid.

Anode: 
$$Cu_{(s)} \longrightarrow Cu^{2+}_{(aq)} + 2e^{\Theta}$$
 (Oxidation)

Cathode:  $Cu^{2+}_{(aq)} + 2e^{\Theta} \longrightarrow Cu_{(s)}$  (Reduction)

The impurities of iron, nickel, zinc, and cobalt present in blister copper being more electropositive pass into solution as soluble sulphates, while the impurities of antimony, selenium, tellurium, silver, gold and platinum being less electropositive are not affected by CuSO<sub>4</sub> - H<sub>2</sub>SO<sub>4</sub> solution and hence settle down under the anode as anode mud or anode sludge. The recovery of precious metals such as silver, gold and platinum from the anode mud more than compensates for the high cost of electrolytic refining. Copper thus obtained is 99.95-99.99% pure.

# 1.8.5 VAPOUR PHASE REFINING

Cathode:

Vapour phase refining involves the removal of impurities from the crude metal by:

- 1. Converting the metal into its volatile compound.
- 2. Decomposition of the volatile compound to get pure metal. Hence, the two requirements are:
  - 1. Metal should form a volatile compound with suitable reagent.
  - 2. Volatile compound should decompose easily so that the recovery is easy.

This method is exemplified by the following processes.

# 1.8.5.1 Mond's Process (Thermal Decomposition Method)

It is based on the formation of volatile metal carbonyl, which is then thermally decomposed to get pure metal. It is used for the purification of nickel and iron.

Impure nickel in the form of fine powder is heated in the presence of carbon monoxide at 50-80°C to form volatile nickel carbonyl, [Ni(CO)4], which is then passed over the nickel balls maintained at 180-200°C, where it decomposes liberating metallic nickel (which gets deposited on Ni balls) and CO is circulated through the plant again.

$$Ni_{(s)} + CO_{(g)} \xrightarrow{50-80^{\circ}C} [Ni(CO)_{4(g)}] \xrightarrow{180-200^{\circ}C} Ni_{(S)} + 4CO_{(g)}$$
  
Impure nickel

Note: The temperature required for the formation of volatile compound should be less than the temperature required for its decomposition.

# 1.8.5.2 Van Arkel Method (Filament Growth Method)

It is based on the formation of volatile covalent metal iodide and is used for the purification of those metals which are very difficult to obtain in pure state, e.g. zirconium, titanium, hafnium, vanadium, silicon and beryllium.

Pure, compact zirconium, Zr, was first prepared in 1924 by Van Arkel and De Boer by the reaction between crude zirconium and iodine vapour at 600°C to form volatile zirconium tetraiodide,  $ZrI_4$ .

$$Zr_{(s)} + I_2 \xrightarrow{600^{\circ}C} ZrI_4 \xrightarrow{1800^{\circ}C} Zr_{(S)} + 2I_2$$

Leading Vapour Vapour

The vapours of  $ZrI_4$  were allowed to diffuse on a tungsten filament maintained at 1800°C (Figure 1.16). Decomposition of  $ZrI_4$  occurred and pure Zr was deposited on the filament. Iodine liberated is recycled. Pure zirconium can be obtained by drilling out the filament.

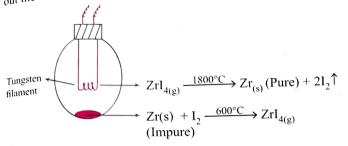


Fig. 1.16 Van Arkel method

Note: Only those metals can be purified by this method whose melting point is greater than 1800°C.

# 1.8.6 KROLL'S PROCESS

This method is used for purification of those metals for whom neither oxide reduction nor electrolysis is suitable for chemical reasons.

Reduction of metal halide by reactive metals such as magnesium, sodium, calcium is employed.

Titanium is an outstanding example of a metal which cannot be prepared by conventional methods because of its high affinity for oxygen.

In Kroll's process, highly purified TiCl<sub>4</sub> is reduced by magnesium (Mg) in an inert atmosphere (argon).

$$TiCl_4 + 2Mg \xrightarrow{1100 \text{ K}} Ti + 2MgCl_2$$

# 1.8.7 PARTING'S PROCESS

This process is employed to remove impurity of copper (Cu) and silver (Ag) from gold (Au) by using  $H_2SO_4$  or  $HNO_3$ .

Gold is not attacked by  $\rm H_2SO_4$  or  $\rm HNO_3$ , but copper and silver dissolve in them, when concentration of gold in the sample is less than 30%. If, however, the gold content in the impure sample is more than 30%, then copper and silver are also not attacked by acid of any strength.

Hence, before acid treatment, impure sample is melted with necessary amount of silver to reduce the gold content to ~25% (quartation).

The resulting alloy after being granualated in water is boiled with  $\rm H_2SO_4/HNO_3$  when silver and copper passes into solution leaving gold behind. Gold is separated and fused with borax and nitre and 100% gold is obtained. It is cast into ingotes.

# 1.8.8 VACUUM ARC FURNACE REFINING

Crude metal made into an electrode is progressively melted in an arc furnace under vacuum. As electrode melts, volatile impurities boil off. The molten metal is chilled by pouring into a water- cooled copper crucible. Refractory metals (with high melting point) such as Ti, Zr, Mo are refined by this method.

# 1.8.9 PYROMETALLURGICAL OXIDATION OR OXIDATIVE REFINING

This method is used when the impurities present in the metal have a greater affinity for  $O_2$  and are more readily oxidised than the metal. This method is usually employed for refining metals such as Pb, Ag, Cu etc. In this method, the molten impure metal is subjected to oxidation by various ways as given below:

# 1.8.9.1 Furnace Refining or Poling

Air is blown through the molten metal to which a suitable flux may be added. Impurities are oxidised and escape as gases (CO<sub>2</sub> etc.) or pass into the slag. Finally the surface of molten metal is covered with low sulphur coke (to prevent oxidation of the metal), and green logs (poles) of wood are introduced into the molten metal and metal is stirred. Hydrocarbon gases escape from the poles and reduce any oxide of the metal which might have been formed; for example Cu, Sn.

### 1.8.9.2 Cupellation

In this method, the molten impure metal is heated in a cupel (boat-shaped dish made of bone ash or cement), and a blast of air is passed over the molten metal. The impurities are oxidised, and the volatile oxides thus produced escape with the blast of air. The pure metal remains in the cupel. For example, the impurity of lead present in silver is removed by cupellation.

# 1.8.9.3 Bessemerisation (Steel Manufacture)

In this method, the impure molten metal is heated in a specially designed furnace and a blast of compressed air is blown through the molten metal. Molten pig iron is purified by this method. The molten pig iron from the blast furnace is taken in a Bessemer converter, and the impurities present in it are oxidised by blast of compressed air.

#### 1.8.10 CHROMATOGRAPHY

It is the most modern and versatile method for separation, purification and testing, the purity of elements and their compounds. **Principle:** It is based on the fact that the *different components of a mixture are adsorbed to different extents on an adsorbent.* 

Chromatography is essentially a physical technique. It consists of two phases: the stationary phase and the mobile phase. The stationary phase can be either a solid (such as alumina, silica gel) or a tightly bound liquid on a solid support (such as paper in which the liquid water is held by the solid cellulose). On the other hand, mobile phase can be a liquid, gas or a supercritical fluid such as CO<sub>2</sub>. Depending upon the physical state of the stationary phase and the moving phase and also on the process of passage of the moving phase, chromatography can be of several types such as column chromatography, partition chromatography, gas chromatography, etc.

Column chromatography: Column chromatography is one of the simplest chromatographic techniques and is widely used. In column chromatography, an adsorbent such as alumina (A1<sub>2</sub>O<sub>3</sub>), silica gel or some ion exchange resin is packed in a column (Figure 1.17). This forms the stationary phase. The mixture to be separated is dissolved in a suitable solvent (mobile phase) and applied to the top of the column. Different components of the mixture are adsorbed to different extents depending upon their polarity.

Later the adsorbed components are extracted (eluted) from the column with a suitable solvent (eluent). The component which is more strongly adsorbed on the column takes longer time to travel through the column than a component which is weakly adsorbed. Thus, the various components of the mixture are separated as they travel through the adsorbent (stationary phase).

This technique is especially suitable for such elements which are available only in minute quantities and the impurities are not very much different in chemical properties from the elements to be purified. Lanthanoids (rare earth elements) are purified by this technique using ion exchange as the adsorbent.

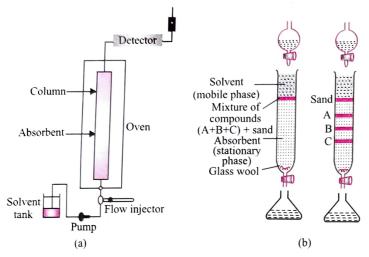


Fig. 1.17 Column chromatography: (a) industrial method and (b) laboratory method

# 1.9 EXTRACTION OF SILVER (Ag)

A few commercially important ore of Ag are as follows:

S.No. Ore		Formula		
1.	Horn silver	AgCl (chiorargyrite) Principal ores		
2.	Argentite	$AgCl (chiorargyrite) Ag_2S (silver glance) Principal ores of Ag$		
3.	Ruby silver	$3Ag_2S \cdot Sb_2S_3$		
4.	Proustite	$Ag_3AsS_3$		
5.	Stromeyerite	Ag <sub>2</sub> S·Cu <sub>2</sub> S (silver copper glance)		

# Extraction of silver (Ag):

- 1. Extraction from silver ores (cyanide process)
  - a. Crushing and concentration: The powdered ore is concentrated by froth flotation method.
  - b. Treatment with NaCN (leaching): The concentrated ore is leached with NaCN solution (0.5%) in presence of air when silver and its salt are converted to soluble

$$Ag_2S + 2NaCN \longrightarrow Na_2S + 2AgCN$$
  
 $AgCN + NaCN \longrightarrow Na[Ag(CN)_2]$ 

Sodium dicyanidoargentate(I) (soluble)

Oxygen in air converts Na<sub>2</sub>S to Na<sub>2</sub>SO<sub>4</sub> and hence reversibility of reaction is checked.

$$4\text{Na}_2\text{S} + 2\text{H}_2\text{O} + 5\text{O}_2(\text{air}) \longrightarrow 2\text{Na}_2\text{SO}_4 + 4\text{NaOH} + 2\text{S}$$

Precipitation of silver: It is done by adding Zn dust (Zn being more electropositive than Ag).

$$2Na[Ag(CN)_{2}] + Zn \longrightarrow Na_{2}[Zn(CN)_{4}] + 2Ag$$

$$2Na[Ag(CN)_{2}] + 4NaOH + Zn$$

$$\longrightarrow 4Na_{2}ZnO_{2} + 4NaCN + 2H_{2}O + 2A_{g}$$

d. Purification (Electrolytic refining)

Electrolyte: AgNO<sub>3</sub> (containing 10% HNO<sub>3</sub>) solution Anode: impure silver

Cathode: thin sheet of pure silver

$$Ag \longrightarrow Ag^{\oplus} + e^{\ominus}$$
 (At anode)  

$$Ag^{\oplus} + e^{\ominus} \longrightarrow Ag \text{ (Pure)}$$
 (At cathode)

Impurities like Zn and Cu pass into solution, while gold (if present) falls down as anode mud.

# 2. Extraction from argentiferous lead

Pb extracted from argentiferous lead contains small quantities of Ag, so it is extracted from it.

- a. Parkes process: It is based on the following facts.
  - i. Molten zinc and lead are immiscible; zinc being lighter forms the upper layer.
  - ii. Silver is more soluble in molten Zn than molten lead
  - iii. Zn-Ag alloy solidifies earlier than molten lead.
  - iv. Zn being volatile can be separated from Ag by distillation.
- b. Pattinson's process: Argentiferous lead is melted and cooled when at first lead gets solidified and thus removed. Entire process is repeated many times till entire mass solidifies. At this stage, Pb-Ag allow containing nearly 2-4% Ag is obtained, which is recovered by cupellation.

# 3. Recovery of Ag and Cu from its alloy:

An alloy of Cu and Ag  $\xrightarrow{\text{dil. HNO}_3}$  AgNO<sub>3</sub> + Cu(NO<sub>3</sub>)<sub>2</sub> • AgNO<sub>3</sub> + Cu(NO<sub>3</sub>)<sub>2</sub>  $\xrightarrow{\Delta}$  AgNO<sub>3</sub> + CuO + 2NO<sub>2</sub>↑

- AgNO<sub>3</sub> and CuO are washed in water. CuO is obtained as residue and the filtrate contains AgNO3. The filtrate is heated very strongly to give silver (Ag).

$$2AgNO_3 \longrightarrow 2Ag + 2NO_2 + O_2$$

The residue is dissolved in dil. H<sub>2</sub>SO<sub>4</sub> to obtain CuSO<sub>4</sub> CuSO<sub>4</sub> is treated with scrap iron to get Cu.

$$Fe + CuSO_4 \longrightarrow Cu + FeSO_4$$

# 1.10 EXTRACTION OF GOLD (Au)

A few commercially important sources of gold are as follows:

S.No.	Ore	Formula
1.	Alluvial sand	Native state, Au (gravel)
2.	Calaverite	AuTe <sub>2</sub>
3.	Sylvanite	AuAgTe <sub>2</sub>

Extraction of gold depends upon the nature of the ore.

1. Extraction of vein gold: Amalgamation process is employed for extraction of gold from hard auriferous quart rocks. It involves the following two steps:

- broken into small pieces by rock crushers and then powdered by means of a battery of stamp mills working in series. Each stamp mill consists of a huge pestle (stamp) and a mortar (die) made up of steel. Each stamp weighs about 1250 lbs and falls through a height of 7.5 inches over the crushed rock on the mortar at the rate of 100 strokes per minute. The stamps are raised by rotating camshaft and then dropped by gravity. The powdered ore is washed out of the stamp mill through the screen by the current of water. The screen allows only fine particles to pass, while bigger particles are retained, which are powdered again.
- b. Amalgamation: The slurry flowing out of the stamp mill is then passed over amalgamated copper plates placed just in front of the stamp mills. The heavier gold particles are retained by mercury to form gold amalgam. The gold amalgam is scrapped off from time to time and distilled in iron retorts when mercury distils over leaving behind pure gold.
- 2. Extraction from gold ores: MacArthur–Forest cyanide process is used for the extraction of gold from the sulphide or telluride ore, which involves the following steps:
  - a. Crushing, grinding, and concentration: The gold ore is crushed and powdered and then concentrated by froth flotation process.
  - **b. Roasting:** The concentrated ore is roasted in excess of air or oxygen when impurities of sulphur, arsenic, and tellurium are oxidised and escape as their volatile oxides.
  - c. Treatment with KCN: The finely powdered roasted ore is taken in large vats made up of cement or iron and having false wooden bottoms with holes. It is then treated with a dilute (0.5%) solution of KCN in presence of excess of air for 24 hrs. As a result, gold dissolves in KCN to form a soluble complex called potassium dicyanidoaurate(I).

$$4 Au + 8KCN + 2H_2O + O_2 \longrightarrow 4K[Au(CN)_2] + 4KOH$$
Potassium
dicyanidoaurate(I)

d. Precipitation of gold: The above solution containing potassium dicyanidoaurate(I) is filtered to remove insoluble impurities and then treated with zinc dust, when gold being less electropositive than zinc gets precipitated.

$$2K[Au(CN)_2] + Zn \longrightarrow K_2[Zn(CN)_4] + 2Au \downarrow$$
  
The precipitated gold is recovered by filtration.

- 3. Refining of gold: Gold obtained by any of the above methods is impure and contains silver, copper, zinc and sometimes lead as impurities. These impurities are removed as follows:
  - a. Cupellation: The impure metal is melted in a cupel in presence of borax and silica and air is passed through the fused mass. Zinc and lead are oxidised and are blown off

while silver and a small amount of Cu remains, which are then removed by the parting process.

b. Parting process: Removal of impurities of silver and copper from gold is called parting. It is carried out by boiling impure gold with either conc. H<sub>2</sub>SO<sub>4</sub> or conc. HNO<sub>3</sub> when copper and silver dissolve while gold remains unaffected.

$$Cu + 2H2SO4 \longrightarrow CuSO4 + SO2 + 2H2O$$

$$2Ag + 2H2SO4 \longrightarrow Ag2SO4 + SO2 + 2H2O$$

It is, however, found that if the percentage of gold in the impure sample is more than 30%, the sample is not attacked by the acid. More silver is, therefore, added to the sample till an alloy containing about 25% of gold is obtained. This is then treated with boiling conc.  $\rm H_2SO_4$  when Ag and Cu dissolve leaving behind gold.

- c. Miller's process (chlorine parting): Parting with chlorine is sometimes used. Impure gold is fused, covered with borax, and dry chlorine gas is passed through it. Gold is unaffected (gold chloride being unstable at high temperatures), while the other metals form chlorides. Silver chloride floats on the surface, whereas the chlorides of other metals (such as Hg, Zn, As etc.) are volatilised. The silver chloride is skimmed off leaving behind only gold.
- d. Electrolytic refining: This method is used when very pure gold is required. The impure gold is made the anode, while a thin sheet of pure gold acts as the cathode. The electrolyte consists of a solution of auric chloride (AuCl<sub>3</sub>) acidified with 10–12% HCl. On passing current of high density, pure gold gets deposited on the cathode.

# 1.11 EXTRACTION OF ZINC (Zn)

A few commercially important ores of zinc are as follows:

S.No.	Ore	Formula
1.	Zinc blende	ZnS
2.	Zincite	ZnO (red oxide)
3.	Zinc spine	ZnAlO <sub>2</sub>
4.	Calamine	ZnCO <sub>3</sub>
5.	Willemite	Zn <sub>2</sub> SiO <sub>4</sub> (ZnSiO <sub>3</sub> ·ZnO)

#### **Extraction of zinc:**

- 1. Concentration: The ore is concentrated first by gravity method and then by froth flotation process. If Fe<sub>2</sub>O<sub>3</sub> is present as an impurity, it is removed by magnetic separation.
- 2. Roasting: The concentrated ore is then roasted at  $900^{\circ}-1000^{\circ}\text{C}$  to convert ZnS and ZnSO<sub>4</sub> to ZnO.  $2\text{ZnS} + 3\text{O}_2 \longrightarrow 2\text{ZnO} + 2\text{SO}_2$

$$ZnS + 2O_2 \longrightarrow ZnSO_4$$

$$ZnSO_4 \longrightarrow 2ZrO + 2SO_2 + O_2$$

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**Note:** If calamine is used as the source, only calcination is required at high temperature.  $ZnCO_3 \longrightarrow ZnO + CO_2$ 

**3. Reduction of coke:** The oxide ZnO is reduced with coke at about 1500°C to obtain metallic zinc.

$$ZnO + C \longrightarrow Zn + CO$$
  
 $ZnO + CO \longrightarrow Zn + CO_2$ 

**4. Electrolytic refining:** Zn thus produced contains impurities like Pb, Cd and Fe. These impurities are removed by liquation. Pure zinc is obtained by electrolysing zinc in presence of acidified ZnSO<sub>4</sub> (ZnSO<sub>4</sub> + dil.H<sub>2</sub>SO<sub>4</sub>) as electrolyte. Impure zinc is made the anode and pure zinc, the cathode.

**Note:** Zinc can also be extracted by electrolytic method. ZnS is first roasted at 700°C to produce ZnO. Then, the oxide ZnO is leached with H<sub>2</sub>SO<sub>4</sub> to convert to sulphate (ZnSO<sub>4</sub>). After removing impurities by treating with milk of lime, ZnSO<sub>4</sub> is acidified and electrolysed to give pure zinc on cathode.

# 1.12 EXTRACTION OF ALUMINIUM (AI)

A few commercially important ores of aluminium are as follows:

S.No.	Ore	Formula
1.	Bauxite	Al <sub>2</sub> O <sub>3</sub> ·2H <sub>2</sub> O (principal ore)
2.	Corundum	$Al_2O_3$
3.	Feldspar	KAlSi <sub>3</sub> O <sub>8</sub> or K <sub>2</sub> O·Al <sub>2</sub> O <sub>3</sub> ·6SiO <sub>2</sub>
4.	Alunite	KAl <sub>3</sub> (SO <sub>4</sub> ) <sub>2</sub> (OH) <sub>6</sub>
5.	Diaspore	$Al_2O_3 \cdot H_2O$
6.	Cryolite	Na <sub>3</sub> AlF <sub>6</sub>
7.	Clay	Al <sub>2</sub> O <sub>3</sub> ·2SiO <sub>2</sub> ·2H <sub>2</sub> O (kaolin)

**Extraction of aluminium:** Electrolytic method from bauxite  $(A1_2O_3 \cdot 2H_2O)$ 

- 1. Purification of bauxite: Bauxite (Al<sub>2</sub>O<sub>3</sub>·2H<sub>2</sub>O) contains mainly Iron oxide and silica as impurity. It is difficult to remove iron or silicon from aluminium, so the ore is purified before hand. It can be achieved by either of the following processes.
  - a. Bayer's process (for ores containing iron oxide as major impurity): Finely grounded ore is roasted at a low temperature to convert FeO to Fe<sub>2</sub>O<sub>3</sub> and digested with a concentrated solution of NaOH in an autoclave. Al<sub>2</sub>O<sub>3</sub> (amphoteric) dissolves forming NaAlO<sub>2</sub>, while Fe<sub>2</sub>O<sub>3</sub> (basic) remains undissolved. Fe<sub>2</sub>O<sub>3</sub> is removed by filtration.

$$Al_2O_3 \cdot 2H_2O + 2NaOH \longrightarrow 2NaAlO_2 + 3H_2O$$

The filtrate containing sodium aluminate is diluted, treated with a seed crystal of pure Al(OH)<sub>3</sub>, and then agitated, when pure Al(OH)<sub>3</sub> is precipitated (by slow hydrolysis).

$$NaAlO_2 + 2H_2O \longrightarrow NaOH + Al(OH)_3 \downarrow$$

The precipitated  $Al(OH)_3$  is filtered, washed and ignited to give pure alumina  $(Al_2O_3)$ .

$$2AI(OH)_3 \xrightarrow{\Delta} AI_2O_3 + 3H_2O$$

b. Serpek's process (for ores containing silica, SiO<sub>2</sub>):

The powdered ore is mixed with carbon and heated to 1800°C in a current of nitrogen, where aluminium nitride is formed. SiO<sub>2</sub> is reduced to silicon, which volatilises away.

$$Al_2O_3 + 3C + N_2 \longrightarrow 2AIN + 3CO$$
  
 $SiO_2 + C \longrightarrow Si + 2CO \uparrow$ 

Aluminium nitride is hydrolysed by water to Al(OH)<sub>3</sub>, which on ignition gives pure alumina.

$$AIN + 2H2O \longrightarrow AI(OH)3 + NH3$$

$$2AI(OH)3 \xrightarrow{1100°C} AI2O3 + 3H2O$$

**c.** Hall's process: Crude bauxite reacts with  $Na_2CO_3$  at  $1000^{\circ}C$  to give sodium aluminate, and impurities  $Fe_2O_3$  and  $SiO_2$  form  $NaFeO_2$  and  $Na_2SiO_3$  respectively.

$$Al_2O_3 + Na_2CO_3 \longrightarrow 2NaAlO_2 + CO_2\uparrow$$

CO<sub>2</sub> at a temperature of around 60°C is passed into sodium aluminate solution producing Al(OH)<sub>2</sub>.

$$2\text{NaAlO}_2 + \text{CO}_2 + 3\text{H}_2\text{O} \longrightarrow 2\text{Al(OH)}_3 + \text{Na}_2\text{CO}_3$$

$$2\text{Al(OH)}_3 \xrightarrow{\Delta} \text{Al}_2\text{O}_3 + 3\text{H}_2\text{O}$$

2. Electrolytic reduction of alumina: Aluminium cannot be isolated by electrolysis of aqueous solution of Al<sub>2</sub>O<sub>3</sub>. Since aluminium is more electropositive than hydrogen, so its electrolysis gives H<sub>2</sub> at cathode.

 $Al_2O_3$  is infusible (MP = 2050°C), so it cannot be electrolysed. So pure alumina dissolved in molten cryolite (Na<sub>3</sub>AlF<sub>6</sub>) containing some CaF<sub>2</sub> or NaF is electrolysed at about 800–1000°C. The electrolysis is carried out in an iron cell lined with graphite (cathode). The anode is a series of graphite rods.

$$AlF_3 \longrightarrow Al^{3+} + 3F^{\Theta}$$

At cathode: 
$$Al^{3+} + 3e^{\Theta} \longrightarrow Al$$

At the same time,  $Al_2O_3$  dissociates into  $Al^{3+}$  and  $O^{2-}$ . Since 'O' is below F in the electronegativity series,  $O^{2-}$  ions are selectively discharged at the anode as oxygen.

At anode: 
$$2Al_2O_3 \longrightarrow 4Al^{3+} + 6O^{2-}$$
$$6O^{2-} \longrightarrow 3O_2 + 12e^{\Theta}$$

The oxygen liberated at the anode combines with the carbon of the anode to form CO and  $CO_2$ , so the anode, which burns away, has to be replaced periodically. Molten Al collects at the bottom of cell (99% pure).

- **3. Electrolytic refining:** The cell layers contain three fused layers:
  - a. The bottom anode layer of an alloy of Al, Cu, Si
  - **b.** The middle layer of cryolite and BaF<sub>2</sub>
  - c. The top cathode layer of pure aluminium.

When a current is passed, Al<sup>3+</sup> ions from the fused middle layer get discharged at the cathode, while an equivalent

amount of aluminium moves into the middle layer. Impurities (Cu etc.) remain at the bottom.

# 1.13 USES OF ALUMINIUM, COPPER, ZINC AND IRON

# 1.13.1 USES OF ALUMINIUM

- 1. Aluminium foils are used for wrapping fine articles like photographic films, pharmaceutical products, cigarettes, chocolates, sweets, etc.
- 2. Aluminium powder, being highly reactive, is used as a reducing agent in aluminothermic process for the extraction of chromium and manganese from their oxides.
- 3. Aluminium is a cheap metal which resists corrosion. Therefore, it is used for making household utensils, cans for drinks, tubes for toothpaste, picture frames, trays, etc. It is used in buildings for making angles for doors, windows, etc.
- 4. Fine dust of aluminium is used for making aluminium paints and lacquers. For example, aluminium powder mixed with linseed oil shines like silver and is called silver paint.
- 5. Being light and good conductor of electricity (on weight to weight basis, Al conducts twice as Cu), aluminium is used for making transmission cables and for winding the moving coils of dynamos or motors.
- **6.** Aluminium powder is used for flashlight bulbs in indoor photography.
- 7. Alloys of aluminium, being light, are very useful as listed below:

S. No.	Alloy	Compo- sition	Important properties	Uses
1.	Aluminium bronze	A1 = 95%, Cu = 5%	Light strong alloy with golden lustre, resistant to corrosion	Coins, utensils, jewellery, picture frames, etc.
2.	Magnalium	A1 = 95%, Mg = 5%	Light, tough, and strong	Light instru- ments, balance beams, pressure cookers, etc.
3.	Duralumin	Al = 95%, Cu = 4%, Mg = 0.5%, Mn = 0.5%	Light, tough, ductile, resistant to corrosive ac- tion	Making aeroplanes, automobile parts, pressure cookers, etc.

# 1.13.2 USES OF COPPER

- 1. Copper being a good conductor of electricity is extensively used for making electric cables and other electrical appliances.
- 2. Copper being a good conductor of heat is used for making utensils, steam pipes, kettles, evaporating pans, calorimeters, etc.
- 3. Manufacture of copper sulphate.

- 4. Electroplating and electrotyping.
- 5. Manufacture of phthalocyanine dyes and pigments.
- **6.** Some important alloys of Cu with their uses are mentioned below.

S. No.	Alloy	Composition	Uses
1.	Brass	Cu = 60-80%, Zn = 40-20%	For castings, condenser tubes, utensils etc.
2.	Bronze	Cu = 75-90%, Sn = 10-25%	For coins, bells, statues etc.
3.	Aluminium bronze	Cu = 90%, Al = 10%	For picture frames, golden powder for pairs.
4.	Bell metal	Cu = 80%, Sn = 20%	For balls and gongs
5.	Monel metal	Cu = 30%, Ni = 67% Fe and Mn = 3%	For acid pumps and acid containers
6.	German silver	Cu = 25-50%, Zn = 25-35%, Ni = 10-35%	For ornaments, resistant wire
7.	Gun metal	Cu = 88%, Sn = 10%, Zn = 2%	For gears, gun barrels

# 1.13.3 USES OF ZINC

- 1. It is used for protecting iron sheets from corrosion or rusting. This process is known as galvanisation.
- 2. Zinc plates and rods are used in batteries and dry cells.
- 3. It is used in laboratory preparation of H<sub>2</sub> gas.
- **4.** Zn dust is used as a reducing agent in the manufacture of dye stuffs, paints, extraction of gold and silver by the cyanide process etc.
- 5. It is used in the preparation of paints like lithopone.
- **6.** Some useful alloys of Zn are as follows

S. No.	Alloy	Composition	Uses
1.	Brass	Cu = 80%, Zn = 20%	For making utensils, wires, castings, condenser tubes.
2.	German silver	Cu = 55%, Zn = 25%, Ni = 20%	For making coins, cooking utensils, statues, etc.
3.	Die casting metal	Zn = 92.5%, Al = 4%, Cu = 3.5%	

#### 1.13.4 USES OF IRON

- 1. Cast iron, which is the most important form of iron, is used for casting stoves, railway sleepers, gutter pipes, toys, etc.
- 2. It is used in the manufacture of wrought iron and steel.
  - a. Wrought iron, being tough and resistant to rusting, is used for making anchors, wires, bolts, nails, railway carriage couplings, and agricultural implements.

**b.** Steel finds a number of uses. Alloy steel is obtained when other metals are added to it. Some alloy steels and their composition, properties, and uses are listed below:

S. No.	Alloy	Compo- sition	Properties	Uses
1.		s Fe = 73% Cr = 18%, Ni = 8% and carbon 1%	Resists corrosion	For making utensils, cutlery, cycles, automobiles, pens, etc.
2.	Nickel steel	Fe = 96-98%, Ni = 2-4%	Resistant to corrosion, hard and	For making cables, automobiles and aeroplane parts.
3.	Chrome	Fe = 96–98%, Cr = 2–4%%	elastic High tensile strength	For making axles, ball bearings, cutting tools and crushing machines.
		Fe = 64%, Ni = 36%	no coef-	For making watches, meter scales, pendulum
5.	. 1		expansion Highly	rods, etc. For making permanent magnets

#### 1.14 FURNACE

Furnace is a device in which high temperature is produced either by burning a fuel or by using electricity. Several types of furnaces are used in the extraction of metals. The important ones are described as follows:

#### 1.14.1 REVERBERATORY FURNACE

This is a kind of furnace (Figure 1.18) in which fuel does not come in direct contact with the charge. The flames are deflected from the roof of the furnace to the charge undergoing reaction. Thus, this furnace can be used for reduction as well as oxidation.

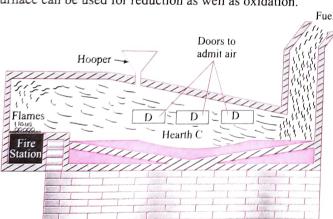


Fig. 1.18 Reverberatory furnace

The furnace consists of three main parts, namely, fire place, hearth and chimney. The fire place is built at one end of the furnace at slightly lower level than that of the hearth. The roof is made slanting and connects with the chimney on the other end. The hot gases from the fire place are reflected by the concave

ceiling over the hearth. The furnace is surrounded on all  $side_s$  by walls of fire bricks. Air supply can be controlled by vents and direct blast.

The furnace is used for smelting (reduction) and roasting of the ores. The reduction is done by the use of some suitable reducing agent. The furnace is used (a) for reducing the roasted tin stone (SnO<sub>2</sub>) to molten tin metal by the use of coke, (b) for roasting the galena ore (PbS) as to convert it into PbO and PbSO<sub>4</sub> by the use of air and (c) for roasting of copper pyrites (CuFeS<sub>2</sub>) as to convert it into Cu<sub>2</sub>O and FeO by means of air.

#### 1.14.2 MUFFLE FURNACE

Muffle furnace (Figure 1.19) is used when high temperature is required and the fuel and its products of combustion are not to be desired to come into contact with the material to be heated. The muffle is a chamber made of refractory material. The muffle is surrounded by hot flames and hot gases all around. In an electric muffle furnace, the closed chamber is surrounded by heating electric coils. Such a furnace is used for the extraction of zinc and for annealing of gold and silver assaying.

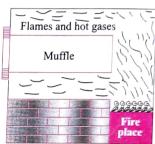


Fig. 1.19 Muffle furnace

#### 1.14.3 ELECTRIC FURNACE

In these furnaces, electrical energy is converted into heat energy. Such furnaces are largely used where cheap power is available and very high temperatures are required and also for carrying electrolytic reduction. The electric furnaces are generally of three types:

- 1. Induction furnace
- 2. Arc furnace
- 3. Resistance furnace
- Induction furnace: In this furnace, the charge lying on the furnace bed or in a crucible constitutes the secondary coil of an induction unit, and the induced currents produced by making and breaking the primary circuit heat up the material.
- 2. Arc furnace: Heat is generated by arcs and a temperature over 3000°C may be obtained. Carbon electrodes are used to carry the current and an arc is struck between them and the charge. Arc furnaces are of two types:
  - a. Direct heat
  - b. Indirect heat

In direct heat arc furnace, arc is used to heat up a gas in which the arc is burning, and in indirect heat arc furnace, the arc burns above the charge, i.e., the arc radiates heat towards the charge.

3. Resistance furnace: Heat is generated by the resistance in the electric circuit. In some cases the material forming the charge may act as the resistance, and in other cases the body of furnace is made up of resistance material and

this material cause heating. In some cases, rods of poorly conducting materials are embedded into the charge, which becomes intensely hot on passage of current.

# 1.15 REFRACTORY MATERIALS

The materials which can withstand very high temperatures without melting or becoming soft are known as refractory materials. These are not affected by slags formed during the extraction of metals. These are used in the form of bricks for the internal linings of furnaces. Refractory materials used are of three types:

- Acid refractories: Silica, quartz, siliceous sandstones etc. are examples.
- Basic refractories: Lime, dolomite, magnesite etc. are examples.
- 3. Neutral refractories: Graphite, chromite, bone ash etc. are examples.

Silica (92% SiO<sub>2</sub>, 2.7% Al<sub>2</sub>O<sub>3</sub>) and quartz can tolerate temperature up to 1750°C, bauxite up to 2000°C, and magnesite, chromite, etc. up to 2200°C. Carbon carbides such as silicon carbide is used as refractory for special purposes.

# 1.16 SUMMARY OF OCCURRENCE AND EXTRACTION OF FEW ELEMENTS

Metal	Occurrence	Extraction Method	Remarks
Lithi- um	Spodumene [(LiAl (SiO <sub>3</sub> ) <sub>2</sub> ]	Electrolysis of fused LiCl with KCl added to it. Li <sup><math>\oplus</math></sup> + $e \rightarrow$ Li	Because of their high reactivity they are extracted under anhydrous condi- tion
So- dium	Rock salt (NaCl), feldspar (Na <sub>3</sub> Al-Si <sub>3</sub> O <sub>8</sub> ), Chile saltpetre (NaNO <sub>3</sub> )	Electrolysis of fused NaCl with CaCl <sub>2</sub> added to it. Na $^{\oplus}$ + $e^{\ominus}$ $\rightarrow$ Na	-do-
Potas- sium	Carnallite (KCl· MgCl <sub>2</sub> ·6H <sub>2</sub> O)	Electrolysis of fused KCl with $CaCl_2$ added to it. $K^{\oplus} + e^{\Theta} \rightarrow K$	-do-
Beryl- lium	Beryl (3BeO· Al <sub>2</sub> O <sub>3</sub> ·6SiO <sub>2</sub> )	Electrolysis of fused BeF <sub>2</sub> with NaF added to it. Be <sup>2+</sup> + $2e^{\Theta}$ Be	-do-
Mag- ne- sium	Carnallite (KCl. MgCl <sub>2</sub> .6H <sub>2</sub> O) Magnesite (MgCO <sub>3</sub> )	Electrolysis of fused $MgCl_2$ with KCl added to it. $Mg^{2+} + 2e^{\Theta} \rightarrow Mg$ Carbon reduction of $MgO$	Reduction using carbon is not possible with alkaline earths as they easily form carbides.

	General Princip	ples and Processes of Isola	ation of Elements 1.31		
Cal- cium	$(CaCO_3),$ $(CaSO_4),$	Electrolysis of fused CaCl <sub>2</sub> and CaF <sub>2</sub> mixture. Ca <sup>2+</sup> + $2e^{\Theta} \rightarrow$ Ca	-do-		
Zinc	Zinc blende (ZnS), calamine (ZnCO <sub>3</sub> ), sphalerite (ZnS)	Reduction of ZnO with C or electroly- sis of ZnSO <sub>4</sub> ZnO + C $\rightarrow$ Zn + CO	Zn metal can be purified by fractional distillation method.		
Nickel	Millerite (NiS)	Reduction of NiO w NiO + 5CO $\rightarrow$ Ni(C Ni(CO) <sub>4</sub> $\rightarrow$ Ni + 4C	$(O)_4 + CO_2$		
Mer- cury	Cinnabar (HgS)	$HgS + O_2 \rightarrow Hg + S$			
Chro- mium	Chromite (FeO.Cr <sub>2</sub> O <sub>3</sub> )	Reduction of $Cr_2O_3$ $Cr_2O_3 + 2Al \rightarrow 2Cr$	+Al <sub>2</sub> O <sub>3</sub>		
Iron	Magnetite (Fe <sub>3</sub> O <sub>4</sub> ), haematite (Fe <sub>2</sub> O <sub>3</sub> )	Reduction of oxides with CO. $Fe_2O_3 + CO \rightarrow 2Fe + 3CO_2$			
Bis- muth	Bismuth glance (Bi <sub>2</sub> O <sub>3</sub> ), bismuthite (Bi <sub>2</sub> O <sub>3</sub> )	Reduction of $Bi_2O_3$ with C. $Bi_2O_3 + 3C \rightarrow 2Bi + 3CO$			
Cobalt	Smattite (CoAs <sub>2</sub> )	Reduction of $Co_3O_4$ $3CO_3O_4 + 3Al \rightarrow 90$	T .		
Stron- tium	Strontianite (SrCO <sub>3</sub> ), celestine (SrSO <sub>4</sub> )	Electrolysis of fused $SrCl_2$ $Sr^{2+} + 2e^{\Theta} \rightarrow Br$			
Bari- um	Witherite (BaCO <sub>3</sub> ), barytes (BaSO <sub>4</sub> )	Electrolysis of fused $Ba^{2+} + 2e^{\Theta} \rightarrow Ba$	ł BaCl <sub>2</sub> .		
Alu- mini- um	Bauxite (Al <sub>2</sub> O <sub>3</sub> . 2H <sub>2</sub> O), cryolite (Na <sub>3</sub> AlF <sub>6</sub> ), aluminosilicates	Electrolysis of $Al_2O_3$ in molten $Na_3AlF_6$ (cryolite) or in $Na_3AlCl_6$ . $Al^{3+} + 3e^{\Theta} \rightarrow Al$	A good source of electricity is needed in the extraction of Al.		
Man- ganese	Pyrolusite (MnO <sub>2</sub> ), Hausmannite (Mn <sub>3</sub> O <sub>4</sub> )	Reduction of oxide with Al or C. $3Mn_3O_4 + 8Al \rightarrow 4Mn + 4Al_2O_3$			

	1	CITICAL ALL Manager No.		
Tita-	Illmenite	Reduction of TiCl <sub>4</sub> with Mg or Na.		
nium	(TiO <sub>2</sub> ·FeO),	$TiCl_4 + 2Mg \rightarrow Ti + 2MgCl_2$		
	rutile			
	(TiO <sub>2</sub> )			
Tin	Cassiterite	Reduction of SnO <sub>2</sub> with C.		
	$(SnO_2)$	$SnO_2 + 2C \rightarrow Sn + 2CO$		
Lead	Galena	Reduction of PbO with C.		
	(PbS)	$PbO + C \rightarrow Pb + CO$		
Cop-	Copper	Partial oxidation of sulphide ore.		
per	pyrites	$2Cu_2O + Cu_2S \rightarrow 6Cu + SO_2$		
	(CuFeS <sub>2</sub> ),			
	cuprite			
	(Cu <sub>2</sub> O)			
Silver	Argentite	Leaching of sulphide ore using NaCN,		
	$(Ag_2S),$	followed by replacement of Ag by Zn.		
	horn silver	$Ag_2S + 4NaCN \rightarrow 2NaAg(CN)_2 + Na_2S$		
	(AgCl),	$2\text{NaAg(CN)}_2 + \text{Zn} \rightarrow 2\text{Ag} + \text{Na}_2\text{Zn(CN)}_4$		
	occur as			
	metal			
Fold	Occurs as	Same method as used in the case of		
	metal	silver.		

#### ILLUSTRATION 1.8

- a. What is a slag?
- b. Give the principle of zone refining?
- c. An ore sample of galena (PbS) is contaminated with zinc blende (ZnS). Give an example of a chemical which can be used to concentrate galena selectively by froth flotation process.
- d. What is meant by the term 'Pyrometallurgy'?

#### Sol.

- **a.** Slag is a easily fusible material formed when gangue still present in the roasted or calcinated ore combines with the flux.
- **b.** When the melt of an impure metal is allowed to cool, the pure metal crystallises out while the impurities remain in the solution.
- **c.** Sodium cyanide, NaCN, can be used to concentrate galena selectively by froth flotation process.
- **d.** The process of extracting the metal by heating the metal oxide with a suitable reducing agent is known as pyrometallurgy.

#### ILLUSTRATION 1.9

- **a.** Indicate the temperature at which carbon can be used as reducing agent for FeO.
- b. Define flux.
- c. Metal usually do not occur in nature as nitrates. Why?
- **d.** Metal such as Cu, Ag, Zn etc. occur in nature as sulphides rather than oxides. Why?

#### Sol.

- a. At 1073 K or above, the standard free energy of formation of CO from C is much below the standard free energy of formation of FeO. Hence, above 1073 K, carbon can reduce FeO to Fe.
- b. Flux is a substance that combines with gangue, which may still be present in the roasted or calcinated ore to form an easily fusible material called slag.
- c. Nitrates of all metals are soluble in water. Hence, if metal nitrates are present in the crust of earth, these would be slowly and gradually washed by rain water into the sea Hence, metals usually do not occur in nature as nitrates.
- d. The cations of Cu, Ag and Zn, i.e. Cu<sup>⊕</sup>, Ag<sup>⊕</sup> and Zn<sup>2</sup> [pseudo inert gas configuration, (ns<sup>2</sup>p<sup>6</sup>d<sup>10</sup>)] have high polarising power and hence easily polarises the bigger sulphide (S<sup>2-</sup>) ion than the small oxide (O<sup>2-</sup>) ion. Hence sulphides of these metals are more stable than the oxides and these metals occur in nature as sulphides rather than oxides.

#### ILLUSTRATION 1.10

- a. Which of the following metals cannot be extracted by the smelting process?Al, Zn, Fe and Pb.
- b. Graphite is used as an anode but not diamond. Give reason.
- c. Give a method for separation of nickel from cobalt?

#### Sol.

- a. Aluminium cannot be extracted by the smelting process because:
  - i. Al is a highly electropositive element and has strong affinity for oxygen. Hence, Al<sub>2</sub>O<sub>3</sub> is a very stable compound and is not reduced by carbon.
  - ii. Al<sub>2</sub>O<sub>3</sub> on heating with carbon forms aluminium carbide (Al<sub>4</sub>C<sub>3</sub>).

$$2Al_2O_3 + 9C \longrightarrow Al_4C_3 + 6CO$$

- b. Graphite is a good conductor of electricity due to presence of free electrons within its layers, which help in conduction of electricity. Hence, graphite can be used as an anode. Whereas, diamond is a bad conductor of electricity due to absence of free electrons in its structure. Hence, diamond cannot be used as an anode.
- c. Nickel (Ni) can be separated from cobalt (Co) by Mond's process. CO is passed over a heated mixture of Ni and Co at 330–350 K, when Ni forms volatile Ni(CO)<sub>4</sub> but Co does not. The volatile Ni(CO)<sub>4</sub> is separated and then heated at 450–470 K to get pure Ni.

$$Ni + 4CO \xrightarrow{330-350 \text{ K}} Ni(CO)_4 \xrightarrow{450-470 \text{ K}} Ni + 4CO$$
Impure

Nickel

Nickel

tetracarbonyl

nickel

# CONCEPT APPLICATION EXERCISE 1.3

- 1. Name the chief ores of tin, iron and aluminium. What methods are employed for the concentration/purification of their ores?
- 2. How do non-metals occur in nature? How are they extracted/isolated from their natural sources?
- 3. Giving appropriate examples (at least three), explain how the reactivity of a metal is related to its mode of occurrence in nature.
- 4. Describe the principle of froth flotation process. What is the role of a stabiliser and of a depressant? Give one example of each.
- 5. Name three ores which are concentrated by froth flotation process. What is a depressant?
- 6. Copper and silver lie below hydrogen in electrochemical series and yet they are found in the combined state as sulphides in nature. Comment.
- 7. Discuss some of the factors which need consideration before deciding on the method of extraction of metal from
- 8. Name three metals which are obtained by the reduction of their oxides though they do not occur as such in the earth's crust.
- 9. What do you understand by the following terms?
  - a. Roasting

b. Calcination

- c. Smelting
- 10. Name the metals which are associated with the following terms in their extraction from their ores:
  - a. Bessemer's converter
- b. Blast furnace
- c. Aluminothermic process d. Magnetic separation
- 11. Name the main steel plants which are operated by the Steel Authority of India.
- 12. Which metals are generally extracted by the electrolytic processes? What positions these metals generally occupy in the periodic table?
- 13. What are necessary conditions for refining a metal by Van Arkel and Mond's process?
- 14. In column chromotography which compounds acts as (i) stationary phase (ii) mobile phase and (iii) which compound is eluted first?
- 15. How Cl<sub>2</sub> is extracted from brine and why external e.m.f. is required in this process.

## Solved Examples

### EXAMPLE 1.1

Why is it advantageous to roast a sulphide ore to the oxide before reduction?

Sol. The standard free energies of formation,  $\Delta G^{\Theta}$  of most of the sulphides are more negative than those of CS<sub>2</sub> and H<sub>2</sub>S (CS<sub>2</sub>, in fact, is an endothermic compound). Therefore, neither carbon nor hydrogen can reduce metal sulphides to metal. In contrast, the standard free energies of formation of oxides are much lower

than that of SO2 and hence oxidation of metal sulphides to metal oxides is thermodynamically favourable. Moreover, the free energies of formation of these metal oxides are less negative than that of CO and hence carbon can easily reduce these oxides to the corresponding metals.

#### EXAMPLE 1.2

The extraction of Au by leaching with NaCN involves both oxidation and reduction. Justify giving equations.

Solo During leaching process, Au is first oxidised to  $Au^{\oplus}$  by  $O_2$ of the air, which then combines with CN ions to form the soluble complex, sodium dicyaniodaurate(I).

$$4Au_{(s)} + 8NaCN_{(aq)} + 2H_2O_{(l)} + O_{2(g)} \longrightarrow$$
Gold (impure)

Gold (impure)

 $4Na[Au(CN)_2]_{(aq)} + 4NaOH_{(aq)}$  Sodium dicyaniodaurate(I) (Soluble complex)

Gold is then extracted from this complex by displacement method using a more electropositive zinc metal. In this reaction, Zn acts as a reducing agent. It reduces Au<sup>®</sup> to Au while it itself gets oxidised to Zn<sup>2+</sup>, which combines with CN<sup>⊖</sup> ions to form a soluble complex, sodium tetracyanidozincate(II).

$$\begin{aligned} 2\text{Na}[\text{Au}(\text{CN})_2]_{(\text{aq})} + Z\text{n}_{(\text{s})} & \longrightarrow 2\,\text{Au}_{(\text{s})} + \text{Na}_2[\text{Zn}(\text{CN})_4]_{(\text{aq})} \\ & \text{Gold} \quad \text{Sodium} \\ & \text{(pure)} \quad \text{tetracyanidozincate}(\text{II}) \end{aligned}$$

Thus, extraction of Au by leaching with NaCN involves both oxidation and reduction.

#### EXAMPLE 1.3

Free energies of formation  $(\Delta, G^{\Theta})$  of MgO(s) and CO<sub>(g)</sub> at 1273 K and 2273 K are given below:

$$\Delta_{f}G^{\Theta} (MgO_{(s)}) = -941 \text{ kJ/mol at } 1273 \text{ K}$$

$$\Delta_{f}G^{\Theta} (MgO_{(s)}) = -314 \text{ kJ/mol at } 2273 \text{ K}$$

$$\Delta_{f}G^{\Theta} (CO_{(g)}) = -439 \text{ kJ/ mol at } 1273 \text{ K}$$

$$\Delta_{f}G^{\Theta} (CO_{(g)}) = -628 \text{ kJ/mol at } 2273 \text{ K}$$

On the basis of above data, predict the temperature at which carbon can be used as a reducing for agent MgO(s).

#### Sol.

$$Mg_{(s)} + \frac{1}{2} O_{2(g)} \longrightarrow MgO_{(s)}; \Delta_f G^{\Theta} = -941 \text{ kJ/mol}^{-1} \dots (i)$$

$$C_{(s)} + \frac{1}{2}O_{2(g)} \longrightarrow 4CO_{(g)}; \ \Delta_f G^{\Theta} = -439 \text{ kJ/mol}^{-1} \quad ...(ii)$$

The redox equation for reduction of MgO to Mg by C can be obtained by subtracting Eq. (i) from Eq. (ii).

Thus, 
$$MgO_{(s)} + C_{(s)} \longrightarrow Mg_{(s)} + CO_{(g)}$$

Since  $\Delta_{\mathcal{G}}^{\Theta}$  of the above reduction reaction is +ve, reduction of MgO by C is not feasible at 1273 K.

#### b. At 2273 K

$$Mg_{(s)} + \frac{1}{2} O_{2(g)} \longrightarrow MgO_{(s)}; \Delta_f G^{\odot} = -314 \text{ kJ/mol}^{-1} \dots (iii)$$

$$C_{(s)} + \frac{1}{2} O_{2(g)} \longrightarrow CO_{(g)}; \Delta_f G^{\Theta} = -628 \text{ kJ/mol}^{-1} \quad \dots \text{(iv)}$$

Substracting Eq. (iii) from Eq. (iv), the redox equation is

$$\begin{aligned} \text{MgO}_{(s)} + \text{C}_{(s)} &\longrightarrow \text{Mg}_{(s)} + \text{CO}_{(g)} \\ \text{and } \Delta_r G^{\ominus} &= \Delta_f G^{\ominus} \text{ (products)} - \Delta_f G^{\ominus} \text{ (reactants)} \\ &= \Delta_f G^{\ominus} \text{CO}_{(g)} - \Delta_f G^{\ominus} \text{MgO}_{(s)} \\ &= (-628) - (-314) = -314 \text{ kJ mol}^{-1} \end{aligned}$$

Since  $\Delta_{r}G^{\Theta}$  for the above reduction reaction is –ve, reduction of MgO by carbon at 2273 K is feasible.

### EXAMPLE 1.4

Give reason: Reduction of Cr<sub>2</sub>O<sub>3</sub> with Al is thermodynamically feasible, yet it does not occur at room temperature.

Sol. 
$$Cr_2O_{3(s)} + 2Al_{(s)} \xrightarrow{\times} 2Cr_{(s)} + Al_2O_{3(s)}$$

The interpretation of  $\Delta_j G^{\Theta}$  is dependent on K ( $\Delta G = -RT \ln K$ ) the equilibrium constant. Since in the abovementioned reaction all the reactants and products are solids at room temperature, there does not exist any equilibrium between the reactants and the products. That is why the reaction does not occur at room temperature. However, at higher temperature, when chromium (Cr) melts, value of  $T\Delta S$  increases  $(\Delta_f G^{\Theta} = \Delta_f H^{\Theta} - T\Delta_f S^{\Theta})$ . As a result,  $\Delta_{\mathcal{G}}^{\Theta}$  becomes more negative and hence the reaction proceeds rapidly.

#### EXAMPLE 1.5

Cinnabar (HgS) and galena (PbS) on roasting often give their respective metals, but zinc blende (ZnS) does not. Give reason.

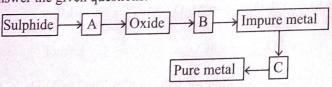
Sol. On roasting, all these sulphide ores are partly converted into their respective oxides. Since the oxides of mercury and lead are unstable while that of zinc is stable, oxides of mercury and lead bring about the reduction of their respective sulphides to the corresponding metals, but zinc oxide does not reduce ZnS to Zn.

$$\begin{array}{c} \text{HgS} + \text{HgO} \xrightarrow{\Delta} 3\text{Hg} + \text{SO}_2 \\ \text{(Unstable)} \\ \text{PbS} + \text{PbO} \xrightarrow{\Delta} \text{Pb} + \text{SO}_2 \\ \text{(Unstable)} \end{array}$$

$$ZnS + ZnO \xrightarrow{\longrightarrow} 3Zn + SO_2$$
(Stable)

#### EXAMPLE 1.6

From the following flowsheet for the extraction of pure metal, answer the given questions.



- Step A is:
  - a. Roasting
- b. Smelting
- c. Calcination
- d. Bessemerisaion
- ii. Step B (reduction) can be carried out by using:
  - a. Carbon
- b. More electropositive element
- c. Both of these
- d. None of these
- iii. Impure Cu metal is also obtained:
  - a. By self-reduction during roasting of CuS
  - b. By reduction of CuO with H,

- c. By reduction of CuO with Al
- d. By electrolysis of Cu<sup>2+</sup> solution
- iv. Some of the following metals are obtained by electrolysis of their fused salts: Al, Na, Cu, Ag, Mg, Ca. These metals are:
  - a. Cu, Ag
- b. Al, Na, Cu
- c. Ag, Mg, Ca
- d. Al, Na, Mg, Ca
- v. Reduction of oxides to elements with carbon generally takes place at high temperature, hence Al is used in aluminothermite process. It is because:
  - a. Al is more electropositive than the other metals (to be formed by reduction).
  - b. Al has maximum affinity for oxygen.
  - c. Reduction is highly exothermic, and the heat liberated makes the process spontaneous.
  - d. Reduction is highly endothermic, and the heat absorbed makes the process spontaneous.
- vi. Following reaction is not involved in thermite process:
  - a.  $3Mn_3O_4 + 8A1 \longrightarrow 9Mn + 4Al_2O_3$
  - b.  $Cr_2O_3 + 2Al \longrightarrow Al_2O_3 + 2Cr$
  - c.  $2\text{Fe} + \text{Al}_2\text{O}_3 \longrightarrow 2\text{Al} + \text{Fe}_2\text{O}_3$
  - d.  $B_2O_3 + 2A1 \longrightarrow 2B + Al_2O_3$
- vii. Match column (A) (process) with column (B) (electrolyte)

	A (Process)		B (Electrolyte)
I	Down's cells process	W	Fused MgCl <sub>2</sub>
II	Dow sea water process	X	Fused (Al <sub>2</sub> O <sub>3</sub> + Na <sub>3</sub> AlF <sub>6</sub> )
III	Hall-Heroult process	Y	Fused KHF <sub>2</sub>
IV	Moissan process	Z	Fused (40% NaCl + 60% CaCl <sub>2</sub> )

Choose the correct answer:

I II III IV

I II III IV

a. Z W X Y

b. X Y W Z

c. W Z X Y

d. X Z W Y

viii. Match the method in column (X) with related reaction in column (Y).

Method (X)			Method (Y)
Ī.	Mond's process	A	$Cr_2O_3 + 2Al \longrightarrow Al_2O_3 + 2Cr$
II	van Arkel– deBoer process	В	$TiCl4 + 2Mg \xrightarrow{1000-1150^{\circ}C} Ti + 2MgCl2$
III	Thermite process	С	$Ni(CO)_4 \xrightarrow{230^{\circ}C} Ni + 4CO$
IV	Kroll process	D	$2CuO + CuS \longrightarrow 3Cu + SO_2$
V	Self reduction	Е	$ZrI_4 \xrightarrow{\Delta} Zr + 2I_2$

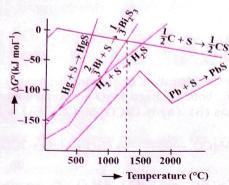
Choose the correct option:

	I.	Ш	. 111	IV	٧
a	A	В	C	D	Ε
b	D	C	В	Α	Е
С	C	Ε	Α	В	D
d	В	D	Е	C	В

iv. d i. a ii. c iii, a, b Sal viii. c v. a. c vi.c vii. a

#### EXAMPLE 1.7

The Ellingham diagram for a number of metallic sulphides is reproduced below.



Answer the questions given below:

- i. Formation of which of the sulphides is not spontaneous?
  - a. HgS

b. Bi,S,

c. PbS

- d. CS,
- ii. Which occurs to minimum extent in nature?

  - a. HgS

b. HaS

c. Bi<sub>2</sub>S<sub>2</sub>

- d. CS<sub>2</sub>
- iii. Which of the following sulphides can be reduced to metal by H<sub>2</sub> at about 1000°C?
  - a. HgS

b. PbS

- c. Bi,S,
- d. All of these

#### Sol.

- (i) (c)  $\Delta_f G^{\odot}$  for PbS is lowest (i.e., more negative) therefore its formation is most spontaneous.
- (ii) (d)  $\Delta_r G^{\Theta}$  for CS<sub>2</sub> is more –ve value at high temperature. This implies that formation of CS<sub>2</sub> is very stable and does not decomposes at high temperature.

Since its formation from C & S, is very stable, so CS<sub>2</sub> exist in nature to minimum extent.

(iii) (b) At  $1000^{\circ}$ C,  $\Delta_f G^{\ominus}$  (H<sub>2</sub>S) >  $\Delta_f G^{\ominus}$  (PbS) therefore PbS can be reduced to Pb by H<sub>2</sub>

 $PbS + H_2 \rightarrow Pb + H_2S$ 

#### EXAMPLE 1.8

Questions given below are based on the given diagram for extractive metallurgy.

- i. At what approximate temperature, zinc and carbon have equal affinity for oxygen?
  - a. 1000°C
- b. 1500°C

c. 500°C

- d. 1200°C
- ii. At this temperature  $\Delta_{\mathcal{L}}G^{\ominus}$  of the reaction is

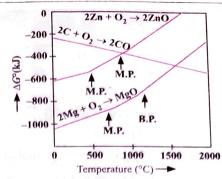
$$ZnO + C \longrightarrow Zn + CO$$

a. -ve

b. +ve

c. Zero

d. Nothing can be said



iii. To make the following reduction process spontaneous temperature should be:

$$ZnO + C \longrightarrow Zn + CO$$

- a. < 1000°C
- b > 1000°C
- c. < 500°C
- d. > 500°C but < 1000°C
- iv. At 1100°C, which reaction is spontaneous to a maximum extent?
  - a.  $MgO + C \longrightarrow Mg + CO$
  - b.  $ZnO + C \longrightarrow Zn + CO$
  - c.  $MgO + Zn \longrightarrow Mg + ZnO$
  - d.  $ZnO + Mg \longrightarrow MgO + Zn$
- v. This method is known as:
  - a. Pyrometallurgy
- b. Parametallurgy
- c. Hydrometallurgy
- d. Semimetallurgy

#### Sol.

- i. (a) At ~1000°C, lines (C, CO) and (Zn, ZnO) intersect: at this temperature zinc and carbon have equal affinity for oxygen.
- ii. (c) At  $\sim$ 1000°C, since Zn and C have equal affinity for O<sub>2</sub>,  $\Delta_{\cdot}G^{\ominus}$  of the reaction is zero.

$$ZnO + C \longrightarrow Zn + CO$$

iii. (b) To make the reaction

$$ZnO + C \longrightarrow Zn + CO$$

to proceed in forward direction, temperature should be greater than 1000°C.

iv. (d) At 1100°C,  $\Delta_{..}G^{\odot}$  for the reaction

$$ZnO + Mg \longrightarrow MgO + Zn$$

has highest negative value, hence this reaction will be spontaneous to a maximum.

v. (a)

#### EXAMPLE 1.9

At high temperature, carbon reacts with water to produce a mixture of CO and H<sub>2</sub>.

$$C + H_2O \xrightarrow{\text{Red heat}} CO + H_2$$

CO is separated from H2 and then used to separate Ni from CO by forming a volatile compound, nickel tetracarbonyl (Ni(CO)<sub>4</sub>).

$$Ni + 4CO \longrightarrow Ni(CO)_4$$

- a. Formation of volatile Ni(CO)<sub>4</sub> and its subsequent heating give pure Ni. Name the process involved.
- b. How many moles of Ni(CO)<sub>4</sub> could be obtained from CO produced by the reaction of 75.0 g of carbon?

#### 1.36 Inorganic Chemistry

a. Mond's process.

**b.** 
$$C + H_2O \longrightarrow CO + H_2$$
  
 $12 g$   $18 g$   $12 + 16$   $2 g$   
 $= 28 g$ 

12 g of C reacts to produce 28 g of CO

75 g of C will react to produce

$$\frac{28}{12}$$
 × 75 g of CO = 175 g of CO =  $\frac{175}{28}$  mol of CO  
= 6.25 moles of CO

 $Ni + 4CO \longrightarrow Ni(CO)_4$ 

Since 4 mol of CO produces 1 mol of Ni(CO)<sub>4</sub>,

6.25 mol of CO will produce

 $\frac{1}{4}$  × 6.25 mol of Ni(CO)<sub>4</sub> = 1.5625 mol of Ni(CO)<sub>4</sub>.

Hence, 1.5625 mol of Ni(CO)<sub>4</sub> could be obtained from CO produced by the reaction of 75.0 g of carbon.

#### EXAMPLE 1.10

$$A \xrightarrow{Calcination} CaO + MgO + (B)$$

Colourless gas

When the colourless gas (B) is passed through lime water, initially a milky solution is obtained and on excess passage of gas (B) through the lime water, milkiness disappears.

i. (A) is:

a. CaCO<sub>3</sub>

b. MgCO<sub>3</sub>

c. CaCO<sub>3</sub>·MgCO<sub>3</sub> d. CaSO<sub>4</sub>·MgCO<sub>3</sub>

ii. (B) is

a. CO,

b. SO<sub>2</sub>

d. SO<sub>2</sub>

iii. Name of the product (A) is:

a. Dolomite

b. Limestone

c. Magnesite

d. Malachite

iv. Lime water is

a. CaO

b. Ca(OH)

c. CaCO<sub>3</sub>

d. CaCO3·Ca(OH)2

v. Milkiness of lime water solution disappears due to the formation of:

a. CaCO<sub>3</sub>

b. Ca(HCO<sub>3</sub>)<sub>2</sub>

c. Ca(OH)<sub>2</sub>

d. CaCl

Sol. Since on calcination, i.e., heating the ore (A) in limited supply of O2, both CaO and MgO are formed along with a colourless gas (B). (A) is CaCO<sub>3</sub>·MgCO<sub>3</sub>. (A) is known as dolomite.

$$CaCO_3 \cdot MgCO_3 \xrightarrow{Calcination} CaO + MgO + 2CO_2$$

$$CO_2 + Ca(OH)_2 \longrightarrow CaCO_3 + H_2O$$

Lime water

$${\rm CaCO_3} + {\rm H_2O} + {\rm CO_2} {\longrightarrow} {\rm Ca(HCO_3)_2}$$

Milkiness disappears

On passing CO<sub>2</sub> through lime water [Ca(OH)<sub>2</sub>] solution, initially lime water turns milky due to formation of CaCO<sub>3</sub>, which is insoluble in water. On excess passage of CO2 gas through lime water, milkiness disappears due to formation of Ca(HCO<sub>2</sub>) Hence,

i. c; A is CaCO<sub>3</sub>·MgCO<sub>3</sub>

ii. a; B is CO<sub>2</sub>

iii. a; CaCO<sub>3</sub>·MgCO<sub>3</sub> is known as dolomite.

iv. b; Limewater is Ca(OH)<sub>2</sub> solution.

v. b; Milkiness disappears due to formation of Ca(HCO<sub>3</sub>)<sub>2</sub>.

## Exercises

#### Single Correct Answer Type

#### **Extraction of Metals Metallurgy**

- 1. The most abundant metal in the earth crust is
  - (1) Al

(2) Fe

(3) Ca

- (4) Na
- 2. The term "nuggets" refer to
  - (1) An ore of Zn
  - (2) An ore of boron
  - (3) An ore which contains metal in the free state and lumps of almost pure metals are found in them.
  - (4) The elements present in the 'core' are collectively known as "nuggets".
- 3. Which metal is generally found is native state?
  - (1) Cu

(2) Au

(3) Al

- (4) Fe
- 4. A mineral is called ore if:
  - (1) a metal can be extracted from it.
  - (2) a metal can not be extracted from it.
  - (3) a metal can be extracted profitably from it.
  - (4) the metal present in the mineral is costly.
- 5. Which of the following is true?
  - (1) All ores are minerals
  - (2) All minerals are ores
  - (3) A mineral cannot be an ore
  - (4) An ore cannot be a mineral
- 6. The impurities present is the mineral are called
  - (1) flux

(2) gangue

(3) alloy

- (4) slag
- 7. Gold is extracted using:
  - (1) Amalgamation process
- (2) Carbon reduction process
- (3) Electrolytic process
- (4) Oxidation process
- 8. Carbon reduction is used for the extraction of:
  - (1) Fe

(2) K

(3) Al

- (4) None of these
- 9. Which is not a basic flux?
  - (1) CaCO<sub>3</sub>

(2) CaO

(3) SiO<sub>2</sub>

- (4) None of these
- 10. Metallurgy is the process of:
  - (1) Concentrating the ore
  - (2) Roasting of the ore
  - (3) Adding carbon to the ore
  - (4) Extracting the metal from the ore
- 11. An essential constituent of analgam is:
  - (1) Hg

(2) Ag

(3) Au

- (4) Al
- 12. Which element is not purified by zone refining?

(1) Ge

(2) Si

(3) Ga

- (4) Ni
- 13. Which element is found in human body?
  - (i) Fe

(ii) Mg

(iii) Ca

- (iv) Al
- (1) Fe, Ca, Mg
- (2) Al, Mg, Ca
- (3) Fe, Ca
- (4) Ca, Mg
- 14. Amongst the following groups of oxides, the group containing oxides that cannot be reduced by carbon to give the respective metals is
  - (1) Cu<sub>2</sub>O, SnO<sub>2</sub>
- (2) Fe<sub>2</sub>O<sub>3</sub>, ZnO
- (3) CaO, K<sub>2</sub>O
- (4) PbO, Fe<sub>3</sub>O<sub>4</sub>
- 15. Slag coming out at the bottom of a blast furnace during extraction of iron from its ore is used in making
  - (1) Fertilisers
- (2) Roads
- (3) Plastics
- (4) Glass moulds
- 16. Regions in which metals are found in earth is called
  - (1) Lithophile
- (2) Atmophile
- (3) Calcophile
- (4) Siderophile
- 17. Which furnace can be used to get temperature above 3000°C?
  - (1) Blast furnace
- (2) Reverberatory furnace (4) None of the above
- (3) Arc furnace
- 18. Which is known as 'blister copper'?
  - (1) Pure copper
- (2) 98% copper
- (3) Alloy of copper
- (4) Ore of copper
- 19. Which process represents the following change,

$$Ti + 2I_2 \longrightarrow TiI_4 \longrightarrow Ti + 2I_2$$
?

- (1) Zone refining
- (2) Mond's process
- (3) Van Arkel method
- (4) Poling
- 20. Following equation represents a method of purification of nickel by

Ni + 4CO 
$$\xrightarrow{320 \text{ K}}$$
 Ni(CO)<sub>4</sub>  $\xrightarrow{420 \text{ K}}$  Ni + 4CO Pure

- (1) Mond's process
- (2) Van Arkel method
- (3) Zone refining
- (4) Cupellation
- 21. The rocks formed by the solidification of magma over the years are (2) Sedimentary rocks
  - (1) Igneous rocks

(3) Metamorphic rocks

- (4) None of these
- 22. The impurities associated with the ore after mining are collectively called
  - (1) Flux

- (2) Slag
- (3) Minerals
- (4) Gangue
- 23. An ore after levigation is found to have acidic impurities. Which of the following can be used as flux during smelting operation? (2) CaCO<sub>3</sub>
  - (1) H<sub>2</sub>SO<sub>4</sub>

(3) SiO<sub>2</sub>

(4) Both CaCO3 and SiO3

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<b>24.</b> The process in which me is called	tal oxide is reduced to metal by Al	36. Heating of ore sulphur is called	ed		impurity of
(1) Smelting	(2) Aluminothermy	(1) Calcination	•	) Roasting	
(3) Hydrothermy	(4) No specific name	(3) Smelting	(4	) None of these	
25. Extraction of silver from	Ag <sub>2</sub> S by the use of sodium cyanide	<b>37.</b> Corundum is	,_		
is an example of		$(1) SrO_2$		$^{2}) Al_{2}O_{3}$	
(1) Roasting	(2) Hydrometallurgy	$(3) CaCl_2$		l) Cu <sub>2</sub> Cl <sub>2</sub>	
(3) Electrometallurgy	(4) Smelting.	38. Which ore ca	n be best conc	centrated by fro	oth flotation
	netals can be extracted by smelting?	process?	(1	() Coggitamita	^
(1) Aluminium	(2) Magnesium	(1) Malachite	`	2) Cassiterite	
(3) Iron	(4) None of these	(3) Galena	`	4) Magnetite	
27. The most abundant elem-		39. The substance			
(1) Nitrogen	(2) Oxygen	(1) Sea shells	`	2) Dolomite	
(3) Iron	(4) Magnesium	(3) Marble sta		4) Calcined gyp:	sum
	g processes involve the roasting	40. The incorrect			
process?	0	` /	and siderite are c		
$(1) ZnCO_3 \longrightarrow ZnO + C$		. , –	and cuprite are or		
(2) $Fe_2O_3 + 3C \longrightarrow 2Fe$		( )	e and iron pyrite		
$(3) 2PbS + 3O_2 \longrightarrow 2Pb$		` /	and azurite are o		
$(4) \operatorname{Al}_2 \operatorname{O}_3 \cdot 2\operatorname{H}_2 \operatorname{O} \longrightarrow \operatorname{Al}_2$	$O_3 + 2H_2O$ ist in free state in nature because	<b>41.</b> Composition			
these are	ist in free state in nature because	(1) CuCO <sub>3</sub> ·Cu		2) Cu(HCO <sub>3</sub> ) <sub>2</sub> ·(	- 2
(1) Very reactive		-	-	4) CuCO <sub>3</sub> ·Cu(C	$(H)_2$
(2) Very volatile		42. Select the cor	rect statement:		
(3) Metallic in nature		( )	n and roasting		
(4) Highly electronegative	re elements		nd small roastin	ig takes place i	n small bla
· · · · · · · · · · · · · · · · · · ·	cess for beneficiation of ores, the	furnace		-111	. 11.1.1
ore particles float because		(2) Calcination furnace	n and roasting t	ake place only	in small blas
(1) They are light				111	1
(2) Their surface is not ea	sily wetted by water	(3) Calcinatio	n and roasting ta	ke place only in	reverberator
(3) They bear electrostation		(4) All are con	moot		
(4) They are insoluble				-11	. 11. 11.
31. The salt which is least lik	ely to be found in minerals is	43. During smelt	th impurities to		
(1) Chloride	(2) Sulphate		estance is called	o ioiiii a iusio	ic mass. 11
(3) Sulphide	(4) Nitrate	(1) Flux	C150 BG	(3) Gangue (	4) Ore
•	eneficiation processes is used for	44. The process of			
the mineral Al <sub>2</sub> O <sub>3</sub> ·2H <sub>2</sub> O?	energia processes is used for		mical reagent fo		
(1) Froth flotation	(2) Leaching		ore electropositiv		
(3) Liquation	(4) Magnetic separation	(1) Electrome	1 4 5	(2) Hydrometal	
33. In aluminothermite proces		(3) Electro re		(4) Zone refinir	
(1) Oxidising agent	(2) Flux	45. Complexes for	~	• /	_
		I. Mond's n	rocess for purific	eation of nickel	aic
(3) Reducing agent	(4) Solder	II. Removal	of lead poisoning	a from the had	
	ed for increasing concentration of	III. Cvanide r	process for extra	g itom the body	
the:	(2) C 1 :		ation process for		nc from gale
(1) Horn silver	(2) Calcite	ore by usi	ng depressant	separation of Z	ns from gaid
(3) Haematite	(4) Magnesite	I	II	III	137
-	re usually concentrated by froth	-			IV
•	ne of the following sulphide ores		[Pb(EDTA)] <sup>2-</sup>		$[Zn(CN)_2]$
offers an exception and is of			$[Pb(EDTA)]^{2-}$		$[Zn(CN)_4]$
(1) Galena	(2) Copper pyrite	$(3) Ni(CO)_6$	[Pb(EDTA)] <sup>4-</sup>	$[Ag(CN)_2]^{\Theta}$	$[Zn(CN)_6]$
(3) Sphalerite	(4) Argentite		[Pb(EDTA)] <sup>2-</sup>		$[Zn(CN)_4]$

- 46. Casseterite ore consists of magnetic impurity named as (1) Chromite
  - (2) Wolframite
  - (3) Magnetite
- (4) Limonite
- 47. Which of the following process is not involved in the extraction of Fe?
  - (1) Gravity separation
- (2) Leaching
- (3) Roasting
- (4) Carbon reduction
- 48. Chalcogens are
  - (1) Hydrocarbons
  - (2) Ore-forming elements
  - (3) Oxide-forming elements
  - (4) Those having ability to catenate
- 49. The oxidation states of Cu and Fe in chalcopyrite are, respectively,
  - (1) +2, +2

(2) +1, +2

(3) + 1, +3

- (4) +2, +1
- 50. Copper can be extracted by hydrometallurgy but not zinc because
  - (1) Copper is comparatively less active metal as its reduction potential is high. It can be displaced from solutions of Cu<sup>2+</sup> ion by more active metals
  - (2) Zn displaced from solution of Zn<sup>2+</sup> ion, a more reactive metal than it, but then readily reacts with water forming their corresponding ions and evolve hydrogen gas
  - (3) Both (a) and (b) are correct
  - (4) Copper can never be extracted by hydrometallurgy
- 51. Which of the following statement is correct?
  - (1) Roasting is unnecessarily done for Fe extraction because there is no sulphide ore
  - (2) In the smelting step of Cu extraction, reduction of the ore takes place
  - (3) Ores may not be mineral
  - (4) Sphalerite is the ore of zinc
- **52.** Consider the following statements:

Roasting is carried out to

- a. Convert sulphide to oxide and sulphate
- b. Remove water of hydration
- c. Melt the ore
- d. Remove arsenic and sulphur impurities

Of these statements:

- (1) a, b and c are correct
- (2) a and d are correct
- (3) a, b and d are correct
- (4) b, c and d are correct.

#### Ellingham Diagram

- 53. Select the correct statement.
  - (1) Sodium cyanide is used as a depressant to separate lead sulphide from zinc sulphide.
  - (2) Iron can reduce alumina to aluminium metal.
  - (3) Substances which convert infusible impurities present in ores into fusible substances during smelting are called slag.
  - (4) Zirconium is best refined by zone refining method.
- 54. Select the incorrect statement.

- (1) Impurities are more soluble in the melt than in the solid state of the metal.
- (2) In Bessemerisation of sulphide ore of copper, there is self- reduction giving copper metal.
- (3) Mercury is transported in containers made of iron.
- (4) The ore CuFeS<sub>2</sub> is used to extract iron metal.
- (5) It is possible to extract a metal from its oxide if the free energy of formation of the oxide of the reducing agent is lower than that of the oxidising agent.
- 55. Select the incorrect statement.
  - (1) Pig iron is manufactured by using blast furnace.
  - (2) Platinum, indium etc. are known as noble metals because they are inert towards many common reagents.
  - (3) Wrought iron is the purest form of iron.
  - (4) Passivity of iron is due to the formation of thin film of sulphides on its surface.
- 56. Select the correct statement.
  - (1) Phenomenon of removing layers of basic oxides from metals before electroplating is called pickling.
  - (2) In the manufacture of iron from haematite, limestone is added to act as flux.
  - (3) An ore of tin containing FeCrO<sub>4</sub> is concentrated by hydrometallurgy.
  - (4) Both (1) and (2)
- 57. Select the incorrect statement.
  - (1) In froth flotation process, the ore particles float because their surface is hydrophilic.
  - (2) Coating of zinc on iron objects is commonly known as galvanisation.
  - (3) In electrorefining, the impure metal is made anode.
  - (4) All are incorrect.
- 58. Which of the following statements about the advantage of roasting of sulphide ore before reduction is not true?
  - (1)  $\Delta_{i}G^{\Theta}$  of the sulphide is greater than  $CS_{2}$  and  $H_{2}S$
  - (2)  $\Delta_i G^{\Theta}$  is negative for roasting of sulphide ore to oxide
  - (3) Roasting of the sulphide to oxide is thermodynamically feasible
  - (4) Carbon and hydrogen are suitable reducing agents for metal sulphides
- 59. When the sample of Cu with Zn impurity is to be purified by electrolysis, the appropriate electrodes are

#### Cathode

(2) Impure sample

#### Anode

- (1) Pure Zn
- Pure Cu
- (3) Impure Zn
- Pure Cu
- (4) Pure Cu
- Impure sample Impure sample
- 60. During the process of electrorefining of copper, some metals
  - (1) Sn and Ag
- (2) Pb and Zn
- (3) Ag and Au
- (4) Fe and Ni
- 61. Which of the following factors is of no significance for roasting sulphide ores to the oxides and not subjecting the sulphide ores to carbon reduction directly?

present as impurity settle down as anode mud. These are

#### 1.40 Inorganic Chemistry

- (1) CO<sub>2</sub> is more volatile than CS<sub>2</sub>
- (2) Metal sulphides are thermodynamically more stable than CS<sub>2</sub>
- (3) CO<sub>2</sub> is thermodynamically more stable than CS<sub>2</sub>
- (4) Metal sulphides are less stable than the corresponding oxides

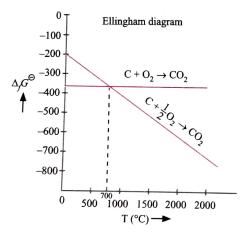
#### 62. Ellingham diagram represents

- (1) Change of  $\Delta G$  with temperature
- (2) Change of  $\Delta H$  with temperature
- (3) Change of  $\Delta G$  with pressure
- (4) Change of  $(\Delta G T\Delta S)$  with temperature
- **63.** To carry out a reduction process, select a temperature so as to make
  - (1)  $\Delta G$  negative
- (2)  $\Delta G$  positive
- (3)  $\Delta H$  negative
- (4)  $\Delta H$  positive

#### 64. Select the correct statement.

- (1) The oxidation of CO into CO<sub>2</sub> will have a negative slope on Ellingham diagram.
- (2) Reduction of metal oxide is difficult if the metal formed is in liquid state at reduction temperature.
- (3) The reactive metals have negative slope for oxidation on Ellingham diagram whereas non-reactive metals have a positive slope
- (4) Reduction of metal oxide is normally less feasible at high temperature.

65.



Which of the following is incorrect on the basis of the above Ellingham diagram for carbon?

- (1) Up to 710°C, the reaction of formation of CO<sub>2</sub> is energetically more favourable, but above 710°C the formation of CO is preferred.
- (2) In principle, carbon can be used to reduce any metal oxide at a sufficiently high temperature.

$$(3) \Delta S[C_{(s)} + 1/2 O_{2(g)} \longrightarrow CO_{(g)}]$$

$$<\Delta S[C_{(s)} + O_{2(g)} \longrightarrow CO_{2(g)}]$$

- (4) Carbon reduces many oxides at elevated temperature because  $\Delta_{\mathcal{L}}G^{\Theta}$  vs temperature line has a negative slope.
- 66. On heating a mixture of Cu<sub>2</sub>O and Cu<sub>2</sub>S, we get
  - (1) Cu + SO<sub>2</sub>
- (2) Cu + SO<sub>3</sub>
- (3) CuO + CuS
- (4) Cu<sub>2</sub>SO<sub>3</sub>

- 67. The method of zone refining of metals is based on the principle of
  - (1) Greater solubility of the impurities in the molten state than in the solid
  - (2) Greater solubility of pure metal than that of impurity
  - (3) Higher melting point of the impurity than that of pure metal
  - (4) Greater noble character of the solid metal than that of the impurity
- 68. Consider the following metallurgical processes:
  - a. Heating impure metal with CO and distilling the resulting volatile carbonyl (BP 43°C) and finally decomposing at 150°C to 230°C to get the pure metal
  - b. Heating the sulphide ore in air until a part is converted to oxide and then further heating in the absence of air to let the oxide react with unchanged sulphide
  - c. Electrolysing the molten electrolyte containing CaCl<sub>2</sub> to obtain the metal

The processes used for obtaining sodium, nickel, and copper are, respectively

- (1) a, b and c
- (2) b, c and a
- (3) c, a and b
- (4) b, a and c
- 69. Complex formation for cyanide method is used for the extraction of
  - (1) Cu

(2) Fe

(3) Hg

- (4) Ag
- **70.** The least stable oxide at room temperature is
  - (1) ZnO

- (2) CuO
- (3) Sb<sub>2</sub>O<sub>3</sub>

- (4) Ag<sub>2</sub>O
- 71. High purity copper metal is obtained by
  - (1) Carbon reduction
- (2) Hydrogen reduction
- (3) Electrolytic reduction
- (4) Thermite process
- 72. The metal extracted by leaching with cyanide is
  - (1) Mg

(2) Ag

(3) Cu

- (4) Na
- 73. When MnO<sub>2</sub> is fused with KOH, a coloured compound is formed; the compound and its colour are
  - (1) K<sub>2</sub>MnO<sub>4</sub>, purple green
- (2) KMnO<sub>4</sub>, purple
- (3) Mn<sub>2</sub>O<sub>3</sub>, brown
- (4) Mn<sub>3</sub>O<sub>4</sub>, black
- 74. By which process Pb and Sn are extracted, respectively?
  - (1) Carbon reduction, self-reduction
  - (2) Self-reduction, carbon reduction
  - (3) Electrolytic reduction, cyanide process
  - (4) Cyanide process, electrolytic reduction
- 75. Extraction of Ag from commercial lead is possible by
  - (1) Parke's process
- (2) Clarke's process
- (3) Pattinson's process
- (4) Electrolytic process
- 76. The chemical composition of slag formed during the smelting process in the extraction of copper is
  - (1) Cu<sub>2</sub>O + FeS
- (2) FeSiO<sub>3</sub>
- (3) CuFeS,
- (4) Cu<sub>2</sub>S + FeO

77. The metal that cannot be obtained by electrolysis of the		91. Blood of human beings contain		
aqueous solution of the	r salts is	(1) Fe	(2) Mg	
(1) Ag	(2) Mg	(3) Co	(4) Al	
(3) Cu	(4) Cr	92. Which is not an ore of	iron?	
78. Ferric oxide in blast fur		(1) Magnetite	(2) Haematite	
(1) C	(2) CO	(3) Limonite	(4) Cuprite	
(3) $H_2$	(4) CO <sub>2</sub>	93. Lepidolite is an ore of		
79. Electric furnaces are line		(1) K	(2) Na	
(1) It melts at a very hig	_	(3) Li	(4) All of these	
(2) It is not affected by a		94. Granulated zinc is obtain		
(3) It has no effect of ele		(1) Suddenly cooling i		
(4) It liberates oxygen of		(2) Adding molten zin		
80. Furnaces are lined with		(3) Heating zinc to 15		
	ing (2) It is refractory and basic	(4) Dropping molten z		
•	icids (4) It gives O <sub>2</sub> on heating	95. Which is not an ore of		
81. The economical and hig furnace lining is	h melting point compound used in	(1) Galena	(2) Cassiterite	
(1) PbO	(2) CaO	(3) Anglesite	(4) Cerussite	
(1) FbO (3) HgO	(4) ZnO		in stone by heating it in a furnace with	
	` '	$(1) CaCO_3$	(2) Coal	
82. In the reverberatory furn (1) The flames are in cor		(3) CaO	(4) Steam	
		97. Spelter is		
	me in contact with the charge	(1) Impure zinc	(2) Impure iron	
(3) Only hot gases come in contact with the charge		(3) Pure zinc	(4) Impure aluminium	
<ul><li>(4) The flames are not at all there</li><li>83. On heating limestone, carbon dioxide is given off. This</li></ul>		98. CO on passing over h	eated nickel gives	
operation in metallurgy i	_	(1) Ni(CO) <sub>4</sub>	(2) NiCO <sub>3</sub>	
(1) Calcination	(2) Roasting	(3) $CO + H_2$	$(4) CO_2 + H_2$	
(3) Smelting	(4) Ore-dressing		in a blast furnace involves all the steps	
. ,	steel by decreasing the amount of	except		
carbon present in it in a	steer by decreasing the amount of	(1) Reduction	(2) Fusion	
(1) Bessemer converter	(2) Pyrite burner	(3) Sublimation	(4) Decomposition	
(3) Blast furnace	(4) None of these		eO in blast furnace, it is converted to	
85. Rutile is an ore of	(1) Itome of mose	Fe <sub>2</sub> O <sub>3</sub> by roasting so		
	(2) Mn		oved as slag with silica	
(1) Ti	(4) Mg		y increase the melting point of charge	
(3) Ca	· / •	(3) It may not evapor		
<b>86.</b> Iron obtained from blast:		(4) None of the above		
(1) Steel	(2) Cast iron	in the Bessemer conv	ion of copper, the reaction taking place	
(3) Wrought iron	(4) Pig iron	(1) $Cu_2S + 2Cu_2O -$		
87. Which does not contain a		$(1) \operatorname{Cu}_2 \operatorname{S} + 2\operatorname{Cu}_2 \operatorname{O} \longrightarrow$ $(2) \operatorname{Cu}_2 \operatorname{O} + \operatorname{FeS} \longrightarrow$		
(1) Bauxite	(2) Corundum			
(3) Diaspore	(4) Dolomite	(3) FeO + SiO <sub>2</sub> $\longrightarrow$ 1		
88. Which is not a silver ore?		(4) None of the above		
(1) Argentite	(2) Siderite	102. Which metal is a liqu		
(3) Horn silver	(4) Ruby silver	(1) Hg	(2) K	
89. Sandstone in some iron of	res is removed by	(3) Na	(4) Ti	
(1) Carbon filters	(2) Compressed air		correct for refining of crude metals?	
	(4) Sulphuric acid	(1) Liquation: tin		
(3) Limestone	pjects is commonly known as	(2) Zone refining: sil		
	(2) Surface coating	(3) Electrolytic refin		
(1) Galvanisation	(4) Hydroplating	(4) Mond's process:	aiuminium	
(3) Electroplating	(4) Hydropianing			

4.40 Terrenia Chamistry			(3) Roasting followed	by self-reduction	
1.42 Inorganic Chemistry  104. Which of the following co	mbination repre	sents the correct	(3) Roasting followed	by reduction with other metal	
matching of metals with the	e most commonl	y employed ores	(4) Roasting followed by		
for their extraction?		,	(1) Hydrogen is used to	o reduce NiO	
Fe Zn	Cu	Al	(1) Hydrogen is used to	ed by Van Arkel method	
(1) Haematite Sphalerite	Copper	Bauxite	(2) Zirconium is femic	alena is concentrated by froth flotation	
to Windle	pyrites Cuprite	Clay	(3) The sulphide ore ga	of iron, flux used is SiO <sub>2</sub>	
<ul><li>(2) Iron pyrites Zincite</li><li>(3) Siderite Calamine</li></ul>	Malachite	Aluminium	(4) In the metallurgy o	and is not used in the metallura.	
(3) Siderile Calamine		phosphate		ocess is not used in the metallurgy of (2) Cu	
(4) Chalcocite Magnetite	Copper	Bauxite	(1) Hg	(2) Cu (4) Fe	
	glance		(3) Pb	` '	
105. Which of the following ber mineral Al <sub>2</sub> O <sub>3</sub> ·2H <sub>2</sub> O?	nefaction proces	s is used for the	ore is treated with con-	o of $Al_2O_3 + SiO_2 + TiO_2 + Fe_2O_3$ . This c. NaOH solution at 500 K and 35 balances and filtered bot. In the filtrest	
(1) Froth flotation	(2) Liquation		pressure for a few not	ars and filtered hot. In the filtrate, the	
(3) Leaching	(4) Magnetic	separation	species present are		
106. Heating mixture of Cu <sub>2</sub> O ar	nd Cu <sub>2</sub> S will giv	e	(1) NaAl(OH) <sub>4</sub> only		
(1) Cu + SO2	(2) Cu + SO <sub>3</sub>		(2) $Na_2Ti(OH)_6$ only	GIO both	
(3) CuO + CuS	(4) Cu <sub>2</sub> SO <sub>3</sub>		(3) NaAl(OH) <sub>4</sub> and Na	a <sub>2</sub> SiO <sub>3</sub> both	
<b>107.</b> $\Delta_i G^{\Theta}$ vs $T$ plot in the Ellingham diagram slopes downward			(4) Na <sub>2</sub> SiO <sub>3</sub> only		
for the reaction			116. Identify the reaction furnace.	that does not take place in a blass	
(1) Mg + $\frac{1}{2}$ O <sub>2</sub> $\longrightarrow$ MgO	(2) $2Ag + \frac{1}{2}O$	$_2 \longrightarrow Ag_2O$	$(1) 2 \text{Fe}_2 \text{O}_3 + 3 \text{C} \longrightarrow 4$	$4\text{Fe} + 3\text{CO}_2$	
	-		$(2) CO_2 + C \longrightarrow 2CO$	•	
$(3) C + \frac{1}{2} O_2 \longrightarrow CO$	(4) CO + $\frac{1}{2}$ O	$_2 \longrightarrow CO_2$	$(3) CaCO_3 \longrightarrow CaO +$	- CO <sub>2</sub>	
00 W/L:-1 C.1 C.1 .	2		(4) $FeO + SiO_2 \longrightarrow FeSiO_3$		
<b>08.</b> Which of the following reafurnace during extraction of	f iron is endothe			orms a water soluble complex with a n of NaCN in the presence of	
$(1) CaCO_3 \longrightarrow CaO + CO_2$	2		(1) Nitrogen	(2) Oxygen	
$(2) 2C + O_2 \longrightarrow 2CO$			(3) Carbon dioxide	(4) Argon	
$(3) C + O_2 \longrightarrow CO_2$				s roasted in excess of air, a mixture o	
$(4) \operatorname{Fe_2O_3} + 3\operatorname{CO} \longrightarrow 2\operatorname{Fe} + 3\operatorname{CO} \longrightarrow 2\operatorname{CO} \longrightarrow 2\operatorname$	+3CO <sub>2</sub>			. FeO is present as impurity. This can	
<b>99.</b> The ore having two differen	t metal atoms is	3	be removed as slag dur	ring reduction of CuO. The flux added	
(1) Haematite	(2) Galena		to form slag is		
(3) Magnetite	(4) Copper py	rites	(1) SiO <sub>2</sub> , which is an a		
0. Which of the following state	ments about the	e reduction is not	(2) Limestone, which	is a basic flux	
true?			(3) SiO <sub>2</sub> , which is the	basic flux	
(1) Roasting of the sulph	ide to the ox	ide is thermo-	(4) CaO, which is a ba	asic flux	
dynamically feasible			119. Gold is extracted by hydrometallurgical process based on		
(2) Carbon and hydrogen a	re suitable redu	acing agents for	property	, and the process cause in	
metal sulphides			(1) Of being electropo	ositive	
(3) The $\Delta_f G^{\ominus}$ is negative f	or roasting of	sulphide ore to	(2) To form complexes	s, which are water soluble	
oxide			(3) Of being less react	tive	
(4) The $\Delta G^{\odot}$ of the sulphide	e is greater that	n those for CS,	(4) To form salts, which		
and H <sub>2</sub> S	6	2	120. Van Arkel method	of purification of metals involve	
. Among the metals Cr, Fe,	Mn, Ti, Ba, ar	nd Mg, the one	converting the metal to	o a	
that cannot be obtained by	reduction of	metal oxide by	(1) Volatile enough sta	able compound	
aluminium ic			(2)	T	

112. Extraction of zinc from zinc blende is achieved by 121. Self-reduction of CuS to Cu can be carried out in (1) Electrolytic reduction (1) Bessemer converter

(2) Roasting followed by reduction with carbon

(2) Fe

(4) Mg

aluminium is

(1) Cr

(3) Mn

(3) Both (1) and (2)

(2) Volatile unstable compound

(4) None of these

(3) Non-volatile stable compound

(2) Blast furnace

(4) None of these

B is a metal. Hence, (A) and (B) are

(1)  $Na_2[Zn(CN)_4]$ , Zn

(2)  $Na[Ag(CN)_2]$ , Ag

(3) Na<sub>2</sub>[Ag(CN)<sub>4</sub>], Ag

(4)  $Na_3[Ag(CN)_4]$ , Ag

123. Find the formula of A

$$ZnS + O_2 \longrightarrow (A) + SO_2$$

 $(1) ZnCO_3$ 

(2) ZnS

(3) ZnSO<sub>4</sub>

(4) ZnCO<sub>3</sub>·3Zn(OH)<sub>2</sub>

124. Four metals and their methods of refinement are given

i. Ni, Cu, Zr, Ga

ii. Electrolysis, Van Arkel process, zone refining, Mond's process

Choose the right method for each:

(1) Ni: Electrolysis; Cu: Van Arkel process; Zr: Zone refining; Ga: Mond's process

(2) Ni: Mond's process; Cu: Electrolysis; Zr: Van Arkel process; Ga: Zone refining

(3) Ni: Mond's process; Cu: Van Arkel process; Zr: Zone refining; Ga: Electrolysis

(4) Ni: Electrolysis; Cu: Zone refining; Zr: Van Arkel process; Ga: Mond's process

125. Which of the following statement is correct regarding Cu extraction?

(1) In the smelting step, carbon reduction takes places

(2) During roasting, Cu<sub>2</sub>S remains almost unaffected

(3) In Bessemer converter, only self-reduction occurs, not slag formation.

(4) Blister formed in the blister Cu is due to dissolved  $CO_2$ 

126. Carbon reduction process is not commercially applicable for which of the following set to oxides to extract the respective metal?

I. ZnO

II.  $Fe_2O_3$ 

III.  $Al_2O_3$ 

IV. SnO<sub>2</sub>

V. MgO

(1) ZnO, Fe<sub>2</sub>O<sub>3</sub>, SnO<sub>2</sub>

(2) ZnO, SnO, MgO

(3) MgO, Al<sub>2</sub>O<sub>3</sub>

(4) MgO, SnO, Al<sub>2</sub>O<sub>3</sub>

127. Which of the following metal can be reduced by carbon reduction as well as self-reduction?

(1) Fe

(2) Al

(3) Pb

(4) None of these

128. The method not used in metallurgy to refine impure metal is:

(1) Mond's process

(2) Van Arkel process

(3) Liquation

(4) All are used

129. Thermite reduction is not used for commercial extraction of the respective metal from which of the following oxides?

(1) Mn<sub>3</sub>O<sub>4</sub>

 $(2) \text{ TiO}_2$ 

 $(3) \operatorname{Fe_2O_3}$ 

 $(4) \operatorname{Cr}_2 \operatorname{O}_3$ 

130. Select the incorrect statement

(1) Iron is the fifth most abundant element in the earth's crust.

(2) Zinc blende is the ore of zinc.

(3) Froth flotation process is generally employed for sulphide ores.

(4) The most abundant metal in earth's crust is aluminium.

131. Select the incorrect statement

(1) Extraction of aluminium from alumina is done by electrometallurgy.

(2) The metals like Si, Ga, etc., which are used in semiconductors, are purified by zone refining.

(3) The purification of crude metal is referred to refining.

(4) Magnesite is an ore of Mn.

132. Select the incorrect statement

(1) The metal present in chlorophyll is Ca

(2) The process of reduction of oxides by aluminium is known as aluminothermy.

(3) The process of removal of gangue from ore is known as concentration of ores.

(4) Aluminium is obtained from A1<sub>2</sub>O<sub>3</sub> by electrolytic reduction.

133. Select the incorrect statement

(1) In the metallurgical process for electrorefining of the metal, the anode is made of impure metal.

(2) Roasting is generally carried out in sulphide ores.

(3) Gold is usually found in quartz mineral.

(4) Metal extracted from sea water is Ca.

134. Select the incorrect statement

 The naturally occurring chemical substances in form of which metals occur in the earth along with impurities are called minerals.

(2) The earthy and siliceous impurities which generally occur with ores are called slag.

(3) Highly reactive elements occur in nature in combined state.

(4) Minerals from which metals are extracted conveniently and economically are called ores.

135. Select the incorrect statement

(1) The complete process of extracting the metal from its ores is called metallurgy.

(2) Calcination is the process of heating the ore strongly in the absence of air.

(3) An ore of tin containing FeCrO<sub>4</sub> is concentrated by electromagnetic separation

(4) Sodium cyanide solution is used to extract Ag or Al from its ores.

136. Select the incorrect statement

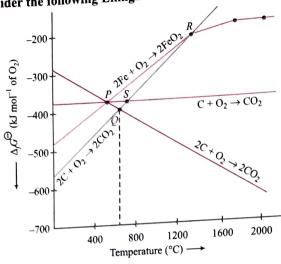
(1) Sulphides ores are concentrated by froth flotation and roasted in excess of air to convert them into their respective oxides.

(2) SiO<sub>2</sub> acts as an acidic flux while CaCO<sub>3</sub> acts as a basic

(3) In the metallurgy of copper, the flux used to remove the basic impurity of FeO is  ${\rm SiO}_2$ 

(4) During extraction of iron from haematite, the flux used is SiO<sub>2</sub>

# Consider the following Ellingham diagram



# 137. Refer to the above Ellingham diagram.

At the temperature corresponding to which of the points in the above given diagram, FeO will be reduced to Fe by coupling the reaction  $2\text{FeO} \rightarrow 2\text{Fe} + \text{O}_2$  with all of the following reactions?

(i) 
$$C + O_2 \rightarrow CO_2$$

(ii) 
$$2C + O_2 \rightarrow 2CO$$

(iii) 
$$2CO + O_2 \rightarrow 2CO_2$$

- (1) Point P & R
- (2) Point Q and R
- (3) Point Q and S
- (4) Point P and S

# 138. Select the incorrect statement about Ellingham diagram.

- (1) According to Ellingham diagram, Aluminium will reduce MgO at temperature below 1350°C.
- (2) All oxides theoretically can not be decomposed to give the metal and  $\rm O_2$ , at sufficiently high temperature.
- (3) At high temperature, a point will be reached where the graph crosses the  $\Delta_f G^{\odot}$  line. Below this temperature,  $\Delta_f G^{\odot}$  of the oxide is negative, so the oxide is stable.
- (4) Any metal will not reduce the oxide of other metals which lie above it in the Ellingham diagram.

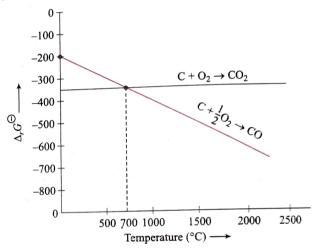
## 139. Select the incorrect statement about the reduction.

- (1) The  $\Delta_{f}G^{\Theta}$  of the sulphide is greater than those for  $CS_2$  and  $H_2S$ .
- (2) C and H<sub>2</sub> are suitable reducing agents for metal sulphides.
- (3) Roasting of the sulphides to the oxides is thermodynamically feasible.
- (4) The  $\Delta G^{\Theta}$  is negative for roasting of sulphide ore to oxide.

# 140. Refer to Ellingham diagram in Q.138. Select the correct option. Below point P, FeO can

- (1) not be reduced by both C and CO.
- (2) be reduced by CO only
- (3) be reduced by both CO and C.
- (4) be reduced by C only.
- 141. Refer to Ellingham diagram in Q.138. Select the correct option. For the reduction of FeO at the temperature at point R is:

- (1)  $\Delta G^{\Theta}$  value for the overall reduction reaction with  $CO_{is}$  negative.
- (2)  $\Delta G^{\odot}$  value for the overall reduction reaction with a mixture of a 1 mol of C and 1 mol  $O_2$  is positive.
- (3)  $\Delta G^{\odot}$  value for the overall reduction reaction with a 2 mol C and 1 mol of  $O_2$  will be positive.
- (4)  $\Delta G^{\odot}$  value for the overall reduction reaction with CO is zero.
- 142. Refer to Ellingham diagram in Q.138. The temperature at which C reduces FeO to give Fe and CO is
  - (1) Above temperature at point P.
  - (2) Above temperature at point P but below temperature at point R.
  - (3) Below temperature at point P.
  - (4) Approximately at temperature corresponding to point p
- 143. On the basis of above Ellingham diagram, select the incorrect statement.



- (1) Carbon can be used to reduce any metal oxide at a high temperature.
- (2) Carbon reduces many oxides at elevated temperature because  $\Delta_i G^{\odot}$  is temperature line with negative slope.
- $(3) \Delta S (C, CO) < \Delta S (C, CO_2)$
- (4) Upto 710°C, formation of CO<sub>2</sub> is more favourable energetically but above 710°C, the formation of CO is preferred.

# Multiple Correct Answers Type

- 1. Metallurgy involves steps:
  - (1) Concentration of ore
- (2) Reduction of ore
- (3) Purification
- (4) Alloy formation
- 2. Which of the following ores is/are oxide ore(s)?
  - (1) Cassiterite
- (2) Bauxite
- (3) Cryolite
- (4) Haematite
- 3. Which of the following are correctly matched?
  - (1) Malachite

(4) Azurite

- $: \mathsf{CuCO_3}{\cdot}\mathsf{Cu(OH)_2}$
- (2) Chalcopyrite
- : CuFeS<sub>2</sub>
- (3) Copper glance
- : Cu<sub>2</sub>S : Cu<sub>2</sub>O

#### 4. Find the correct match:

Column I		Column II	
(1)	Azurite	CuCO <sub>3</sub> ·2Cu(OH) <sub>2</sub>	
(2)	Malachite	Cu(OH) <sub>2</sub> ·CuCO <sub>3</sub>	
(3)	Anglesite	PbSO <sub>4</sub>	
(4)	Chalcocite	Cu <sub>2</sub> S	

- 5. Carnallite is an ore of
  - (1) Sodium
- (2) Potassium
- (3) Magnesium
- (4) Aluminium
- 6. Which is (are) not an ore?
  - (1) Bauxite
- (2) Zinc blende
- (3) Pig iron
- (4) Wrought iron
- 7. Salt which is (are) least likely to find in minerals
  - (1) Acetate
- (2) Nitrate
- (3) Chloride
- (4) Sulphate
- 8. Metal(s) which does/do not form amalgam is/are:
  - (1) Fe

(2) Zn

(3) Ni

- (4) Au
- 9.  $Ca_3(PO_4)_2$  is:
  - (1) Thomas slag
  - (2) Used in cement manufacturing
  - (3) Used in manufacture of phosphorus fertiliser
  - (4) Used as a refractory material
- 10. Which of the following pairs consists of ore of the same metal?
  - (1) Magnesite, cerussite
- (2) Chalcocite, copper pyrites
- (3) Bauxite, corundum
- (4) Anglesite, cerussite
- 11. Froth flotation process used for the concentration of sulphide
  - (1) Is based on the difference in wettability of different minerals
  - (2) Uses sodium ethyl xanthate,  $C_2H_5OCS_2Na$ , as collector
  - (3) Uses NaCN as depressant in the mixture of ZnS and PbS when ZnS forms soluble complex and PbS forms froth
  - (4) Uses pine oil as frothing agent
- 12. Which of the following are correct processes?
  - (1) Fe + Al<sub>2</sub>O<sub>3</sub>  $\longrightarrow$  2Al + Fe<sub>2</sub>O<sub>3</sub>
  - (2) ZnO + C  $\longrightarrow$  Zn + CO
  - (3)  $Cr_2O_3 + 2Al \longrightarrow 2Cr + Al_2O_3$
  - $(4) 2[Ag(CN)_2]^{\Theta} + Zn \longrightarrow 2Ag + [Zn(CN)_4]^{2-}$
- 13. Which of the following reactions occur during calcination?
  - (1)  $CaCO_3 \longrightarrow CaO + CO_2$
  - (2)  $2Al(OH)_3 \longrightarrow Al_2O_3 + 3H_2O$
  - $(3) 4 \text{FeS}_2 + 11 \text{O}_2 \longrightarrow 2 \text{Fe}_2 \text{O}_3 + 8 \text{SO}_2$
  - $(4) Cu<sub>2</sub>S + 2CuO \longrightarrow 4Cu + SO<sub>2</sub>$
- 14. Leaching can be used for extraction of
  - (1) Pb

(2) Al

(3) Ag

- (4) Au
- 15. MgO can be used as a refractory material because

- (1) It is a good electrical insulator
- (2) It is a good conductor of heat
- (3) It has high melting point
- (4) None of the above.
- 16. The extraction of metals from oxide ores involves
  - (1) Reduction with carbon
- (2) Reduction with aluminium
- (3) Electrolytic reduction
- (4) Reduction with CO
- 17. Which of the following oxides cannot be reduced to metal by carbon?
  - (1) ZnO

(2) Al<sub>2</sub>O<sub>3</sub>

(3) CuO

- (4) MgO
- 18. Which of the following statements are correct regarding metallurgy of iron?
  - (1) Coke reduces FeO to Fe above 1073 K
  - (2) CO reduces Fe<sub>2</sub>O<sub>3</sub> to FeO below 1073 K
  - (3) Coke reduces  $Fe_2O_3$  to FeO above 1073 K
  - (4) Coke reduces Fe<sub>2</sub>O<sub>3</sub> to FeO above 1073 K
- 19. The major role of flourspar, CaF<sub>2</sub> which is added in small amount in the electrolytic reduction of  $\mathrm{Al_2O_3}$  dissolved in fused cryolite is
  - (1) To increase the conductivity of the fused mixture
  - (2) To lower the fusion temperature of the melt
  - (3) To act as catalyst
  - (4) To decrease the rate of oxidation of carbon at the anode
- 20. Which is correct process-mineral group in metallurgical extraction?
  - (1) Leaching: Ag
- (2) Van Arkel: Zr
- (3) Liquation: Sn
- (4) Zone refining: Sn
- 21. Tempering of steel
  - (1) Increases mechanical strength
  - (2) Changes ratio of iron in steel
  - (3) Involves heating the steel to appropriate temperature and then cooling it rapidly
  - (4) Decreases mechanical strength
- 22. Out of the following reduction processes:
  - i.  $Fe_2O_3 + 3C \longrightarrow 2Fe + 3CO$
  - ii.  $Cu_2O + C \longrightarrow 2Cu + CO$
  - iii.  $PbO + C \longrightarrow Pb + CO$
  - iv.  $ZnO + C \longrightarrow Zn + CO$

Correct process is/are:

(1)(i)

(2)(ii)

(3) (iii)

- (4) (iv)
- 23. Which out of the following metals can be obtained by electrolysis of the aqueous solution of their salts?
  - (1) Ag

(2) Mg

(3) Au

- (4) Na
- 24. Auto-reduction process is used for the extraction of:
  - (1) Cu

(2) Hg

(3) Pb

- (4) Al
- 25. Disadvantages of using carbon as a reducing agent:
  - (1) High temperature is needed
  - (2) Many metals combine with carbon to form carbides

- (3) Low temperature is needed
- (4) Many metals combine with carbon and do not form carbides
- 26. Select the correct statements:
  - (1) Based on reactivity series, occurrence of certain elements takes place in native state
  - (2) Due to the basic nature of oxides of alkaline earth metals, they combine with atmospheric acidic oxides giving salts
  - (3) Based on reactivity series, occurrence of certain elements takes place in atomic state
  - (4) None is correct
- 27. Which of the following steps are involved in hydrometallurgical process?
  - (1)  $Cu_2S + 2Cu_2O \longrightarrow 6Cu + SO_2$
  - (2)  $CuFeS_2 + 2H_2SO_4 \longrightarrow CuSO_4 + FeSO_4 + 2H_2S$
  - $(3) \operatorname{Ag}_{S} + 2 \operatorname{NaCN} \longrightarrow [\operatorname{Ag}(\operatorname{CN})_{2}]^{\Theta} + \operatorname{Na}_{2} \operatorname{S}$
  - $(4) CuCO<sub>3</sub> + H<sub>2</sub>SO<sub>4</sub> \longrightarrow CuSO<sub>4</sub> + H<sub>2</sub>O + CO<sub>2</sub>$
- 28. The reduction of an oxide by aluminium is not called
  - (1) Ellingham process
  - (2) Goldschmidt's aluminothermite process
  - (3) Kroll's process
  - (4) Van Arkel process
- **29.** For the pyrometallurgical method used for the extraction of copper from sulphide ore, which statements is/are correct?
  - (1) Pyrometallurgy is a dry method
  - (2) It involves concentration by leaching the sulphide ore with dil. H<sub>2</sub>SO<sub>4</sub>
  - (3) It involves concentration of the sulphide ore by froth flotation process
  - (4) It involves concentration by leaching for every ore
- 30. In Fe extraction, the roasting is carried out because
  - (1) All FeO be converted to Fe<sub>2</sub>O<sub>3</sub>
  - (2) The formation of FeSiO<sub>3</sub> slag is prevented
  - (3)  $Fe_2O_3$  does not react with  $SiO_2$  to form slag
  - (4) The formation of slag (CaSiO<sub>3</sub>) is enhanced
- 31. Which of the following metal oxides are reduced by self-reduction method?
  - (1) Cu<sub>2</sub>O

(2) PbO

(3) HgO

- (4) CaO
- **32.** Select the correct statements:
  - (1) In hydrometallurgy, Zn is used as oxidising agent in the purification of Ag from  $[Ag(CN)_2]^{\bigcirc}$ .
  - (2) When pine oil or eucalyptus oil is added into the water, it lowers down the surface tension by which froth is formed
  - (3) Sodium ethyl xanthate is used as collector
  - (4) Basic copper carbonate or PbSO<sub>4</sub> is concentrated by froth flotation method by using an activator
- 33. Select the correct statements for calcination:
  - (1) Carbonate ore is converted in oxide ore
  - (2) Hydrated oxide ore is converted into its oxide ore

- (3) Oxidisable volatile impurities are removed by calcination process
- (4) Only calcination occurs for carbonate or oxide ore
- 34. In the commercial extraction of iron, roasting is adopted because
  - (1) It removes impurities of S, As, and Sb in the form of their elemental vapour
  - (2) It prevents slag formation by Fe<sub>2</sub>O<sub>3</sub>
  - (3) It prevents slag formation by FeO
  - (4) Limonite is converted into its anhydrous form
- 35. Which of the following statements is/are correct?
  - (1) The chemical processes in the production of steel from haematite ore involve reduction followed by oxidation
  - (2) Lead is extracted from its chief ore galena by both carbon reduction as well as self-reduction
  - (3) In Hall-Heroult process, the electrolyte used is a molten mixture of alumina and cryolite or fluorspar
  - (4) Haematite, cassiterite and argentite are oxide ores
- 36. Liquation process may be applied for the purification of
  - (1) Copper
- (2) Tin

(3) Iron

- (4) Lead
- **37.** The anode mud obtained during electrorefining of copper may contain
  - (1) Iron

(2) Magnesium

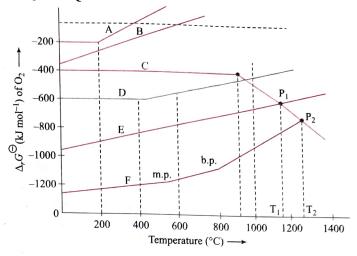
(3) Silver

- (4) Gold
- 38. The extraction of metals from sulphide ore involves
  - (1) Reduction with carbon
- (2) Froth flotation
- (3) Reduction with Al
- (4) Eletrolytic reduction
- 39.  $H_2$  is not widely used as the reducing agent in metallurgical process because
  - (1) Many metals react with  $H_2$  at elevated temperature forming hydrides
  - (2) There is a risk of explosion from  $H_2$  and  $O_2$  present in the air
  - (3) Reducing power of H<sub>2</sub> does not increase with temperature
  - (4) Reducing power of  $H_2$  increases with temperature
- 40. Select the correct statement.
  - (1) Alkali metals are generally extracted by electrolysis of their ores in fused state.
  - (2) Levigation is generally employed for concentration of sulphide ores.
  - (3) Every mineral is an ore, but every ore is not a mineral
  - (4) Slag is a product formed during smelting by combination of flux and impurities.
- 41. Select the correct statement.
  - (1) Alkali metals can be obtained by chemical reduction of their compounds.
  - (2) Sylvine is an ore of potassium.
  - (3) Oxide ores are purified by levigation process.
  - (4) During electrorefining of a metal, impure metal is made anode.
- 42. Select the correct statement.
  - (1) Highly pure metals can be obtained by zone refining.
  - (2) Aluminium is the most abundant metal in the earth's crust.

- (3) Reactive metals occur in native state.
- (4) The process of calcination and roasting is carried out in reverberatory furnace.
- 43. Select the correct statement.
  - (1) In calcination, ore is heated with calcium.
  - (2) Copper is found both in free as well as in combined state in nature.
  - (3) Below 1623 K, Al can reduce MgO to Mg, but above 1623 K, reverse is true.
  - (4) Mond's process is used for purification of titanium.
- 44. Select the correct statements (Ellingham diagram):
  - (1) When temperature is raised, a point will be reached where the graph crosses the  $\Delta_{i}G^{\Theta} = 0$  line. Below this temperature, the free energy of formation of the oxide is negative, so the oxide is stable
  - (2) When the temperature is raised, a point will be reached where the graph crosses the  $\Delta_{r}G^{\odot} = 0$  line. Above this temperature, the free energy of formation of the oxide is positive, and the oxide becomes unstable, and should decompose into the metal and dioxygen
  - (3) Theoretically, all oxides can be decomposed to give the metal and dioxygen if a sufficiently high temperature can be attained
  - (4) Theoretically, all oxides cannot be decomposed to give the metal and dioxygen if a sufficiently high temperature can be attained
- 45. Select the correct statements for Ellingham diagram:
  - (1) Any metal will reduce the oxide of other metals which lie above it in the Ellingham diagram
  - (2) According to Ellingham diagram, Al will not reduce MgO at temperature below 1350°C
  - (3) According to Ellingham diagram, Al will reduce MgO at temperature below 1350°C
  - (4) Any metal will not reduce the oxide of other metals which lie above it in the Ellingham diagram
- 46. Select the correct statements for Ellingham diagram.
  - (1) The slope of the curves of the formation of metal oxide is +ve because  $\Delta G^{\Theta}$  becomes less negative or increases with the rise in temperature
  - (2) Each curve is a straight line except when some change takes place in phase  $(s \rightarrow l \text{ or } l \rightarrow g)$
  - (3) Each curve is not a straight line except when some change takes place in phase  $(s \rightarrow l \text{ or } l \rightarrow g)$
  - (4) The slope of the curves of the formation of metal oxide is -ve because  $\Delta_{i}G^{\Theta}$  becomes less negative or increases with the rise in temperature
- 47. In the leaching of Ag<sub>2</sub>S with NaCN, a stream of air is also passed. It is because of
  - (1) Reversible nature of reaction between Ag<sub>2</sub>S and NaCN
  - (2) Oxidised  $Na_2S$  formed into  $Na_2SO_4$
  - (3) Irreversible nature of reaction between  $Ag_2S$  and NaCN
  - (4) None of the above
- 48. Silver containing lead as an impurity is not purified by

- (1) Poling
- (2) Cupellation
- (3) Levigation
- (4) Distillation

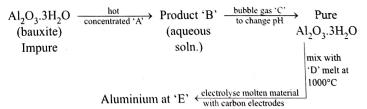
For Q.49 to Q.51



- 49. Refer to the above Ellingham diagram, select correct option.
  - (1) Reduction of E<sub>2</sub>O<sub>3</sub> to E is possible by C below 1000°C
  - (2) At 500°C reduction of oxide of A, B is possible by C.
  - (3) Extraction of D is possible reduction of its oxide by B and C
  - (4) Below 400°C oxide of A should decompose into metal
- 50. Refer to above diagram. Which of the following reaction have  $\Delta G^{\Theta} = 0$ , at temperature  $T_2$  and  $T_1$  respectively.
  - (1)  $FO + C \rightarrow F + CO$
- (2)  $FO + D \rightarrow F + DO$
- $(3) EO + C \rightarrow E + CO$
- (4) EO + D  $\rightarrow$  E + DO
- 51. Refer to above diagram. Select the incorrect statement at 1000°C. Given

$$2D + O_2 \rightarrow 2DO$$
,  $\Delta G^{\odot} = -370 \text{ kJ}$   
 $2C + O_2 \rightarrow 2CO$ ,  $\Delta G^{\odot} = -470 \text{ kJ}$ 

- (1) Reduction of DO is possible by C and metals are obtained in vapour state.
- (2) Reduction of DO is not possible by C
- (3) For reaction DO + C  $\rightarrow$  D + CO,  $\Delta G^{\Theta} = +50 \text{ kJ}$
- (4) Metal C has more affinity for O<sub>2</sub> as compared to D.
- **52.** In the extraction of aluminium metal, one of the process is summarised as follows:



Which of the following entries correctly summarises reagents, electrodes & products of the process?

NaF

Anode

	Α	$\mathbf{B}$	C	D	E
(1)	NaOH	$Al^{3+}$	HF	Na <sub>3</sub> AlF <sub>6</sub>	Cathode

- (2) NaOH NaAlO<sub>2</sub> CO<sub>2</sub> (3)  $H_2SO_4$   $Al_2(SO_4)_3$  NH NA<sub>3</sub>AlF<sub>6</sub> Cathode
- Na<sub>3</sub>AlF<sub>6</sub> (4) NaOH NaAlO<sub>2</sub> CO<sub>2</sub> Cathode

#### 1.48 Inorganic Chemistry

- 53. Of the following reduction processes, correct processes are:
  - (1)  $Fe_2O_3 + C \rightarrow Fe$
- (2)  $ZnO + C \rightarrow Zn$
- $(3) \operatorname{Ca3}(PO_4)_2 + C \to P$
- (4)  $PbO + C \rightarrow Pb$
- 54. Metals which can be extracted by smelting process are:
  - (1) Pb

(2) Fe

(3) Zn

- (4) Al
- 55. Aluminothermy used for the spot welding of large iron structures is based upon the fact that:
  - (1) As compared to iron, aluminium has greater affinity for oxygen
  - (2) As compared to aluminium, iron has greater affinity for
  - (3) Reaction between aluminium and oxygen is endothermic
  - (4) Reaction between iron oxide and aluminium
- 56. Which of the following are true for electrolytic extraction of aluminium?
  - (1) Cathode material contains graphite
  - (2) Anode material contains graphite
  - (3) Cathode reacts away forming CO<sub>2</sub>
  - (4) Anode reacts away forming CO<sub>2</sub>
- 57. The chief reaction(s) occurring in blast furnace during extraction of iron from haematite is/are:
  - (1)  $Fe_2O_3 + 3CO \rightarrow 2Fe + 3CO_2$
  - (2) FeO + SiO<sub>2</sub>  $\rightarrow$  FeSiO<sub>3</sub>
  - $(3) \text{ Fe}_2\text{O}_3 + \text{C} \rightarrow 2\text{Fe} + 3\text{CO}$
  - $(4) \text{ CaO} + \text{SiO}_2 \rightarrow \text{CaSiO}_3$
- **58.** Select correct statement regarding silver extraction process.
  - (1) When the lead-silver alloy is rich in silver, lead is removed by the cupellation process
  - (2) When the lead-silver alloy is rich in lead, lead is removed by parke's or pattinson's process
  - (3) Zinc forms an alloy with lead, from which lead is separated by distillation
  - (4) Zinc forms an alloy with silver, from which zinc is separated by distillation
- 59. Which of the following reduction reactions are actually employed in commercial extraction of metals?
  - (1)  $Fe_2O_3 + 2AI \rightarrow Al_2O_3 + 2Fe$
  - (2) Cr<sub>2</sub>O<sub>3</sub> + 2Al  $\rightarrow$  Al<sub>2</sub>O<sub>3</sub> + 2Cr
  - (3)  $2Na[Au(CN)_2] + Zn \rightarrow Na_2[Zn(CN)_4] + 2Au$
  - (4)  $Cu_2S + Pb \rightarrow Cu + PbS \downarrow$
- **60.** Highly electropositive metals can not be extracted by carbon reduction process because these:
  - (1) Metals combine with carbon to form carbides
  - (2) Metals do not react with carbon
  - (3) Metal oxides are not reduced by carbon
  - (4) Loss of metal is more by vaporisation

## Linked Comprehension Type

### Paragraph 1

Copper is the most noble of first row transition metals and occurs in small deposits in several countries. Ores of copper include chalcanthite (CuSO<sub>4</sub>·5H<sub>2</sub>O), atacanite [Cu<sub>2</sub>Cl(OH)<sub>3</sub>], cuprite (Cu<sub>2</sub>O), copper glance (Cu<sub>2</sub>S), and malachite [Cu<sub>2</sub>(OH)<sub>2</sub>CO<sub>3</sub>] However, 80% of the world copper production comes from the ore chalcopyrite (CuFeS<sub>2</sub>). The extraction of copper from chalcopyrite involves partial roasting, removal of iron and self. reduction.

- 1. Partial roasting of chalcopyrite produces
  - (1) Cu<sub>2</sub>S and FeO
- (2) Cu<sub>2</sub>O and FeO
- (3) Cu<sub>2</sub>O and Fe<sub>2</sub>O<sub>3</sub>
- (4) CuS and Fe<sub>2</sub>O<sub>2</sub>
- 2. Iron is removed from chalcopyrite as
  - (1) FeO

- (2) FeS
- (3) Fe<sub>2</sub>O<sub>3</sub>
- (4) FeSiO<sub>3</sub>
- 3. In self-reduction, the reducing species is
  - (1) S

 $(2) O^{2-}$ 

 $(3) S^{2-}$ 

(4) SO<sub>2</sub>

#### Paragraph 2

Extraction of copper is done using copper pyrites. After roasting the ore is mixed with silica and coke and then smelted in a blast furnace. The matte obtained from the blast furnace is charged into a silica-lined converter. Some silica is also added, and a hot air blast is blown into the mixture to obtain blister copper, which is purified by electrorefining.

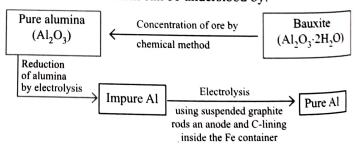
- 4. The chemical formula of copper pyrites is
  - (1) CuFeS<sub>2</sub>
- (2) Cu<sub>2</sub>O

(3) Cu<sub>2</sub>S

- (4) CuCO<sub>3</sub>·Cu(OH)<sub>2</sub>
- 5. The chemical composition of the slag formed during smelting is
  - (1) CuSiO<sub>3</sub>
- (2) FeSiO<sub>3</sub>
- (3) CaSiO<sub>3</sub>
- (4)  $Cu_2O \cdot SiO_2$
- **6.** Coke is added during smelting to
  - (1) Reduce FeO to Fe
  - (2) Reduce Cu<sub>2</sub>O to Cu
  - (3) Check the oxidation of FeO to Fe<sub>2</sub>O<sub>3</sub>
  - (4) Check the oxidation of Cu<sub>2</sub>O to CuO
- 7. Matte is a mixture of
  - (1)  $Cu_2S + FeS$  (small amount)
  - (2)  $FeS + Cu_2S$  (small amount)
  - (3)  $Cu_2O + FeO$  (small amount)
  - (4) FeO +  $Cu_2S$  (small amount)

#### Paragraph 3

Extraction of aluminium can be understood by:



Electrolytic reduction of Al<sub>2</sub>O<sub>3</sub>:

Electrolyte:  $Al_2O_3 + Cryolite + CaF_2$ 

Cathode:

Carbon inside the Fe container

Anode:

Graphite rods

- 8. The purpose of adding cryolite is
  - (1) To remove the impurities as slag
  - (2) To lower the melting point of Al<sub>2</sub>O<sub>3</sub>
  - (3) To decrease the electrical conductivity of pure aluminium
  - (4) To increase the Al percentage in the yield
- 9. Coke powder is spread over the molten electrolyte to
  - (1) Prevent the corrosion of graphite anode
  - (2) Prevent the heat radiation from the surface
  - (3) Prevent the oxidation of molten aluminium by air
  - (4) Both (1) and (2)
- 10. The function of fluorspar (CaF<sub>2</sub>) is
  - (1) To increase the melting point of electrolyte
  - (2) To increase electrolytic conductivity power
  - (3) To remove the impurities as slag
  - (4) All of these
- 11. The molten electrolytes contain  $Na^{\oplus}$ ,  $Al^{3+}$  and  $Ca^{2+}$  but only Al gets deposited at cathode because,
  - (1) Standard reduction potential of Al is more than that of Na and Ca
  - (2) Standard oxidation potential of Al is more than that of
  - (3) Graphite reacts only with Al3+ and not with Na and
  - (4) Discharge potential of  $Al^{3+}$  is higher than  $Na^{\oplus}$  and  $Ca^{2+}$

#### Paragraph 4

Roasting is a process in which the ore (mostly sulphide) is heated strongly in the presence of excess of air. The heating should be done at a temperature below the melting point of the ore.

- 12. Select the correct statement:
  - (1) Roasting removes easily oxidisable volatile impurities like arsenic as As<sub>2</sub>O<sub>3</sub>, antimony as Sb<sub>2</sub>O<sub>3</sub>, and sulphur as
  - (2) The release of SO<sub>2</sub> (in roasting process) has been a serious air pollution problem
  - (3) In roasting process, if temperature is fairly low (about 500°C) and the concentration of SO<sub>2</sub> in the gaseous environment is more, sulphate may be produced, that is stable, and high temperature is needed to decompose it
  - (4) All are correct
- 13.  $2PbS + 3O_2 \longrightarrow A + 2SO_2$

The name of A is

- (1) Litharge
- (2) Galena
- (3) Sesquioxide
- (4) None of these
- 14. Sometimes roasting may not bring about complete oxidation:

$$2\text{CuFeS}_2 + 4\text{O}_2 \longrightarrow \text{A} + 2\text{FeO} + 3\text{SO}_2$$

Find out A:

(1) Cu<sub>2</sub>O

(2) CuO

(3) Cu<sub>2</sub>O

(4) CuS

### Paragraph 5

Lead obtained from galena (PbS) by air reduction or carbon reduction process contains base metal (Cu, Bi, Sn, As) as impurities, due to the which lead becomes hard and brittle.

15. Parke's process is also called

- (1) Softening process
- (2) Desilverisation method
- (3) Cupellation
- (4) None of these
- 16. Cupellation is used for purification of
  - (1) Pb (3) Zn

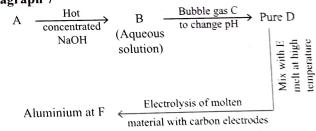
- (2) Ag (4) Fe
- 17. Ag can be obtained from purified Zn-Ag alloy by
  - (1) Distillation
- (2) Poling
- (3) Liquation
- (4) Reduction
- 18. Zn-Ag alloy formed in the upper layer of molten lead is skimmed off from the surface of the molten lead by perforated ladles. This alloy contains lead as impurity. This impurity of Pb is removed by
  - (1) Distillation
- (2) Cupellation
- (3) Liquation
- (4) Bett's electrolysis

#### Paragraph 6

Lead obtained from galena ore (PbS) by air reduction or carbon reduction process contains base metal (Cu, Bi, As, Sn, Zn) as impurities.

- 19. The removal of the impurity of Ag from the commercial lead is called
  - (1) Desilverization of lead
- (2) Softening process
- (3) Bett's electrolysis
- (4) Cupellation
- 20. The electrolyte used for electrolysis of Pb is
  - $(1) PbSO_4 + H_2SO_4$
- (2) PbCl<sub>2</sub> + HCl
- (3) PbSiF6 +  $H_2$ SiF<sub>6</sub>
- (4) None of these
- 21. Gelatin acts as addition agent in electrolysis of Pb. In the presence of gelatin, Pb becomes
  - (1) Hard and brittle
- (2) Soft and useless
- (3) Smooth and uniform
- (4) Only brittle

Paragraph 7



- **22.** A is
  - (1) CuFeS<sub>2</sub>
- (2) MgCl<sub>2</sub>·6H<sub>2</sub>O
- $(3) Al_2O_3 \cdot 2H_2O$
- (4) CuS

- **23.** B is:
  - $(1) Na[Al(OH)_4]$
- (2) NaOH
- $(3) H_2SO_4$
- $(4) Al_2O_3$

- **24.** C is
  - (1) CO,

(2) SO,

(3) SO<sub>3</sub>

(4) NO<sub>2</sub>

- **25.** E is
  - (1) Na<sub>3</sub>GeF<sub>6</sub>
- (2) Na<sub>3</sub>AlF<sub>6</sub>
- (3) Al<sub>2</sub>O<sub>3</sub>
- (4) None of these

- **26.** F is
  - (1) Cathode

- (2) Anode
- (3) Electrolyte
- (4) None of these

#### 1.50 Inorganic Chemistry

#### Paragraph 8

$$\begin{array}{c}
A + NaCN & \stackrel{Air}{\longleftarrow} B + Na_2S & \stackrel{O_2}{\longrightarrow} C \\
\text{(Sulphide ore)} & (Complex)
\end{array}$$

#### **27.** A is

(1) As<sub>2</sub>S

(2) CuS

- (3) Na<sub>2</sub>S
- (4) HgS

#### 28. Composition of B is

- (1)  $Na[Ag(CN)_2]$
- (2) Na<sub>2</sub>[Ag(CN)<sub>2</sub>]
- $(3) \text{Na}[\text{Ag}(\text{CN})_4]$
- (4) Na<sub>3</sub>[Ag(CN)<sub>2</sub>]

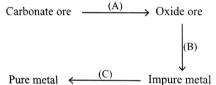
#### 29. B is

- (1) Ferromagnetic
- (2) Paramagnetic
- (3) Linear complex
- (4) Coordination number of central atom is 4

#### **30.** C is

- (1) Na<sub>2</sub>SO<sub>4</sub>
- (2) Na<sub>2</sub>SO<sub>3</sub>
- (3) Na<sub>2</sub>O
- (4) Na<sub>2</sub>O<sub>2</sub>

#### Paragraph 9



#### 31. Name the process (A)

- (1) Roasting
- (2) Smelting
- (3) Calcination
- (4) Reduction

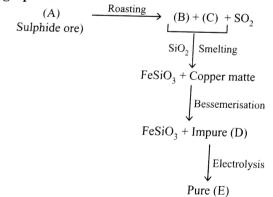
#### 32. Name the process (B)

- (1) Reduction
- (2) Roasting
- (3) Mond's process
- (4) Van Arkel process

#### **33.** Name the process (C)

- (1) Reduction
- (2) Zone-refining
- (3) Roasting
- (4) Calcination

#### Paragraph 10



#### 34. Identify (A)

(1) CuS

- (2) FeS<sub>2</sub>
- (3) CuFeS<sub>2</sub>
- $(4) \operatorname{Fe}_3 O_4$

#### **35.** Identify (B) and (C):

- (1) FeS + FeO
- (2) FeO +  $Cu_2S$
- (3) FeS + Cu<sub>2</sub>O
- (4) Cu<sub>2</sub>O + Cu<sub>2</sub>S

- 36. Composition of copper matte is
  - (1) Cu<sub>2</sub>S + FeS (small amount)
  - (2)  $Cu_2O + FeS$  (small amount)
  - (3)  $Cu_2S + FeSO_4$  (small amount)
  - (4)  $Cu_2S + FeO$  (small amount)
- **37.** Identify (E):
  - (1) Blister Cu
- (2) Pig iron

(3) FeO

- (4) Wrought iron
- **38.** Pure (E) is
  - (1) Cu

(2) Fe

(3) S

 $(4) O_{2}$ 

#### Paragraph 11

Chief ore of Zn is ZnS. The ore is concentrated by froth flotation process and then heated in air to convert ZnS to ZnO.

$$2ZnS + 3O_2 \longrightarrow 2ZnO + 2SO_2$$

··· (i)

ZnO, thus formed is treated with dilute H<sub>2</sub>SO<sub>4</sub>.

$$ZnO + H_2SO_4 \longrightarrow ZnSO_4 + H_2O$$

... (ii)

On electrolysis of ZnSO<sub>4(aq)</sub>, Zn metal is produced.

$$2ZnSO_4 + H_2O \longrightarrow 2Zn + 2H_2SO_4 + O_2$$

... (iii)

- 39. What mass of Zn will be obtained from an ore containing 225 kg of ZnS? (Zn = 65, S = 32, O = 16, H = 1)
  - (1) 102 kg
- (2) 151 kg
- (3) 112 kg
- (4) 134 kg
- 40. ZnO on dissolution in NaOH gives
  - (1) Na<sub>2</sub>ZnO<sub>2</sub>
- (2) NaZnO<sub>2</sub>
- $(3) \text{NaZn}(OH)_4$
- (4) NaZn<sub>2</sub>O<sub>3</sub>
- **41.** How many kilomoles of NaOH are required to dissolve all the ZnO produced in reaction (ii)?
  - (1) 1.16

(2) 2.32

(3) 4.64

- (4) 9.28
- **42.** What volume of 98%  $H_2SO_4$  (by weight, density = 1.8 g/mL) is required in step (ii)?
  - (1) 120 L

- (2) 129 L
- (3) 1.40 L
- (4) 150 L

### Matrix Match Type

This section contains questions each with two columns–I and II. Match the items given in column I with that in column II.

d Vac	Column I		Column II
a.	Azurite	i	Sulphide of iron
b.	Malachite	ii.	Sulphide of copper
c.	Chalcopyrites	iii.	Oxides of copper
d.	Cuprite	iv.	Ore containing
e.	Magnesite	v.	Ore of magnesium
f.	Dolomite	vi.	Carbonate ore

_	Column I Iron pyrites Fool's gold Haematite Galena		Column II
	And the last of th	i.	Fe <sub>2</sub> O <sub>3</sub>
a.		ii.	FeS <sub>2</sub>
b. 		iii.	Sulphide ore
c.		iv.	Al <sub>2</sub> O <sub>3</sub>
d.	Galena	IV.	2
e.	Corundum	V.	Concentrated by froth flotation process
ſ.	Bauxite	vi.	Al <sub>2</sub> O <sub>3</sub> ·2H <sub>2</sub> O

	Column I	Column II		
a.	Mond's process	i.	Refining of Ag	
b.	Thermite process	ii.	Extraction of Cr	
c.	Poling	iii.	Refining of Cu	
d.	Cupellation	iv.	Refining of Zr	
e.	Van Arkel method	v.	Extraction and purification of Ni	
f.	Carbon reduction method	vi.	Iron	

Column I  a. Diaspore  b. Bauxite  c. Corundum  d. Indian saltpetre	Column II		
2.	Diaspore	i.	Al <sub>2</sub> O <sub>3</sub>
b.	Bauxite	ii.	KNO <sub>3</sub>
c.	Corundum	iii.	CaCO <sub>3</sub> ·MgCO <sub>3</sub>
d.	Indian saltpetre	iv.	Al <sub>2</sub> O <sub>3</sub> ·2H <sub>2</sub> O
e.	Carnallite	v.	$Al_2O_3\cdot H_2O$
f.	Dolomite	vi.	KCl·MgCl <sub>2</sub> ·6H <sub>2</sub> O

	Column I	Column II			
a.	Mond's process	i.	Purification of Ge		
b.	Van Arkel method	ii.	Purification of Ni		

c.	Zone refining	iii.	Extraction of Au
d.	Polling	iv.	Purification of Ti
e.	Cupellation	v.	Refining of Ag
f.	Cyanide process	vi.	Purification of copper

Bara	Column I	Column II		
a.	Gypsum	i.	Hg	
b.	Cinnabar	ii.	Pb	
c.	Galena	iii.	Ca	
d.	Argentite	iv.	Al	
e.	Corundum	v.	Mg	
f.	Carnallite	iv.	Ag	

	Column I	90 (90)	Column II		
a.	Copper pyrites	i.	Fluoride ore		
b.	Cryolite	ii.	Sulphate ore		
c.	Rock salt	iii.	Oxide ore		
d.	Alumina	iv.	Sulphide ore		
e.	Dolomite	v.	Chloride ore		
f.	Gypsum	vi.	Carbonate ore		

	Column I		Column II
a.	Chile saltpetre	i.	Mg
b.	Pyrolusite	ii.	Pb
c.	Kiesserite	iii.	Be
d.	Anglesite	iv.	Na
e.	Beryl	<b>v.</b>	Mn
f.	Rutile	vi.	Ti

# 9. Match the items given in Column I with that in Column II and III

Column I		umn I Column II			Column III
<b>a</b> .	Froth floatation method	i.	Used to seperate ZnS and PbS	p.	The crude metal is heated in evacuated vessel with I <sub>2</sub> . The metal iodide is decomposed on electrically heating to give pure metal
b.	Depressants	ii.	Method is bassed on the principle that the impurities are more soluble in the melt than in solid state of metal	q.	Used for removing gangue from sulphide ores
c.	Zone refining method	iii.	Collectors (like pine oils, fatty acids) and stabilisers (like, aniline, cresols) are added	r.	NaCN is added
d.	van Arkel method	iv.	This method is used to remove all $O_2$ and $N_2$ present in the form of impurity in metals like Zr and Ti	s.	Method is useful for producing semiconductors of high purity, eg; Ge Si, B, Ga and In

Answer the questions given below by appropriately matching the information given in three Column of the following table.

	Column I		Column II		Column III
-	Metals		Occurrence		Common method of Extraction
a.	Zn	i.	Haematite	p.	Roasting followed by reduction with coke. The metal may be purified by fractional distillation
b.	Cu	· ii.	Calamine	q.	Roasting of sulphide ore partially and reduction. It is self reduction in a specially designed converter.  H <sub>2</sub> SO <sub>4</sub> leaching is also used in hydrometallurgy from low grade ores
c.	Fe	iii.	Cryolite	r.	Electrolysis of oxide ore dissolved in molten salt. Good source of electricity is required
d.	Al	iv.	Malachite	s.	Reduction of the oxide with CO and coke in Blast furnace at 2170 K.

- 10. For the ore SPHALERITE, CORRECT combination is:
  - (1) a-ii-p
- (2) b-iv-q

- (3) c-i-s
- (4) d-iii-r
- 11. For the ore MAGNETITE, CORRECT combination is:
  - (1) a-ii-p
- (2) b-iv-q

(3) c-i-s

- (4) d-iii-r
- 12. For the ore BAUXITE, CORRECT combination is:
  - (1) a-ii-p
- (2) d-iii-r
- (3) b-iv-q
- (4) c-i-s
- 13. For the ore COPPER PYRITES, CORRECT combination is:
  - (1) a-ii-p
- (2) b-iv-q

(3) c-i-s

(4) b-iv-q

#### Numerical Value Type



- 1. In the bauxite ore, what is the value of x?
- 2. Carnallite consists of how many different compounds?
- 3. In Goldschmidt's aluminothermic process, thermite mixture contains \_\_\_\_\_ parts of Fe<sub>2</sub>O<sub>3</sub> and one part of aluminium.
- **4.** What is the value of x in  $CaSO_4 \cdot xH_2O$ , gypsum?
- 5. How many cyanide ions are involved in the following chemical equation?

$$Au + CN^{\ominus} + H_2O + O_2 \longrightarrow [Au(CN)_2]^{\ominus} + \overset{\ominus}{OH}$$

6. How many of the following metals can be refined by vapour phase refining?

7. Amongst the following elements, how many occurs in the earth's crust in the native state?

- 8. Amongst the following, how many ores can be concentrated by froth flotation process:
- Galena, sphalerite, cassiterite, calamine, chalcocite, haematite, argentite
- 9. Amongst the following, how many ores are roasted to convert them into their corresponding metal oxides, alumina, zinc blende, iron pyrites, copper pyrites, galena.

10. How many of the following are oxide ores

Calamine, cuprite, zincite, chalcocite, haematite, bauxite magnetite, cassiterite

- 11. How many ores are sulphide ores from the given ores? Azurite, chalcoite, iron pyrites, limonite
- 12. How many metals are commercially purified by Van Arkel method from the given metals?

13. How many metals are commercially purified by electrolysis method from the given metals?

14. Find the number of following reactions which are involved in roasting process:

i. 
$$S_8 + 8O_2 \xrightarrow{\Delta} 8SO_2 \uparrow$$

ii. 
$$P_4 + 5O_2 \xrightarrow{\Delta} P_4O_{10} \uparrow$$

iii. 
$$4As + 3O_2 \xrightarrow{\Delta} 2As_2O_3 \uparrow$$

iv. 
$$2ZnS + 3O \xrightarrow{\Delta} 2ZnO + 2SO_2 \uparrow$$

v. 
$$ZnCO_3 \xrightarrow{\Delta} 4ZnO + CO_2 \uparrow$$

15. Find the number of reaction from the given reactions which can show calcination process:

i. 
$$CaCO_3 \cdot MgCO_3 \xrightarrow{\Delta} CaO + MgO + CO_5$$

ii. 
$$CuCO_3 \cdot Cu(OH)_2 \xrightarrow{\Delta} 2CuO + H_2O + CO_2$$

iii. 
$$Al_2O_3 \cdot 2H_2O \xrightarrow{\Delta} Al_2O_3 + 2H_2O$$

iv. 
$$2Cu_2S + 3O_2 \xrightarrow{\Delta} 2Cu_2O + 2SO_2$$

16. How many metallic ores are concentrated by magnetic separation method from the given ores?

Cassiterite, pyrolusite, rutile, magnetite, galena, cinnabar.

17. Find the number of metal oxides which are decomposed on normal heating from the given oxides:

$$Na_2O$$
,  $Al_2O_3$ , PbO,  $Ag_2O$ , HgO

- 18. Find the number of basic flux from the given compounds: SiO<sub>2</sub>, MgO, Cab, FeO, B<sub>2</sub>O<sub>3</sub>, CaCO<sub>3</sub>
- 19. Find the number of metals from the given metals which can be commercially purified by zone refining methods:

Cu, Fe, Sn, Au, K, Na

21. Find the number of acidic flux from the given compounds: CaCO<sub>3</sub>, Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub>, MgSiO<sub>3</sub>, FeSiO<sub>3</sub>, P<sub>2</sub>O<sub>5</sub>

22. How many reactions can show slag formation process from the given reactions?

i.  $SiO_2 + CaO \longrightarrow CaSiO_3$ 

ii.  $FeO + SiO_2 \longrightarrow FeSiO_3$ 

iii.  $CaO + P_2O_5 \longrightarrow Ca_3(PO_4)_2$ 

iv.  $Cr_2O_3 + 2Al \longrightarrow Al_2O_3 + 2Cr$ 

v.  $MgCO_3 + SiO_2 \longrightarrow MgSiO_3 + CO_2$ 

23. How many metals are commercially extracted by electrometallury from the given metals?

Al, Mg, Na, K, Ag, Hg, Ti, Th, Zr, B

24. How many metals are commercially extracted by hydrometallurgy from the given metals:

Ag, Mn, In, Cr, Pb, Au

25. How many metals are commercially reduced by Goldschmidt's aluminothermic process from the given metals?

Na, Pb, Al, Mn, Sn

**26.** Find the number of metals which are commercially reduced by self-reduction from the given metals:

Fe, Al, Zn, Sn, Pb, Hg, Cu

**27.** Find the number of metals which are commercially reduced by carbon reduction method from the given metals:

Ag, Cr, Mn, Sn, Zn, Fe

# **Archives**

#### JEE MAIN

#### Single Correct Answer Type

- 1. Mond's process is used for preparing
  - (1) Ni

(2) H<sub>2</sub>SO<sub>4</sub>

(3) NH<sub>3</sub>

- $(4) \text{ HNO}_3$
- (AIEEE 2010)

Gold is extracted by hydrometallurgical process based on its property

- (1) of being electropositive
- (2) of being less reactive
- (3) to form complexes which are water soluble

(4) to form salts which are water soluble (AIEEE 2012)

- 3. Roasting of sulphides gives the gas X as a by-product. This is a colorless gas produce choking smell of burnt sulphur, and causes great damage to respiratory organs as a result of acid rain. Its aqueous solution is acidic and acts as a reducing agent and it has never been isolated. The gas X is
  - (1) SO<sub>2</sub>

(2) CO.

(3) SO<sub>3</sub>

 $(4) H_2S$ 

(**JEE Main 2013**)

- 4. In the context of the Hall-Heroult process for the extraction of Al, which of the following statements is false?
  - (1) CO and CO<sub>2</sub> are produced in this process
  - (2) Al<sub>2</sub>O<sub>3</sub> is mixed with CaF<sub>2</sub> which lowers the melting point of the mixture and brings conductivity
  - (3) Al<sup>3+</sup> is reduced at the cathode to form Al
  - (4) Na<sub>3</sub>AlF<sub>6</sub> serves as the electrolyte

(**JEE Main 2015**)

- 5. Which one of the following ores is best concentrated by froth floatation method?
  - (1) Malachite
- (2) Mågnetite

- (3) Siderite
- (4) Galena

(**JEE Main 2016**)

- 6. When metal 'M' is treated with NaOH, a white gelatinous precipitate 'X' is obtained, which is soluble in excess of NaOH. Compound 'X' when heated strongly gives an oxide which is used in chromatography as an adsorbent. The metal 'M' is
  - (1) Ca

(2) Al

(3) Fe

(4) Zn

(JEE Main 2018)

#### JEE ADVANCED

#### **Single Correct Answer Type**

- 1. Oxidation states of the metal in the minerals haematite and magnetite, respectively, are
  - (1) II, III in haematite and III in magnetite
  - (2) II, III in haematite and II in magnetite
  - (3) II in haematite and II, III in magnetite
  - (4) III in haematite and II, III in magnetite (IIT-JEE 2011)
- 2. Sulfide ores are common for the metals.
  - (1) Ag, Cu and Pb
- (2) Ag, Cu and Sn
- (3) Ag, Mg and Pb
- (4) Al, Cu and Pb

(JEE Advanced 2013)

- 3. Which series of reactions correctly chemical reactions related to iron and its compound
  - (1)  $Fe \xrightarrow{Cl_2, \text{ heat}} FeCl_3 \xrightarrow{\text{heat, air}} FeCl_2 \xrightarrow{Zn} Fe$
  - (2) Fe  $\xrightarrow{O_2$ , heat  $\rightarrow$  Fe<sub>3</sub>O<sub>4</sub>  $\xrightarrow{CO, 600^{\circ}C}$  FeCl<sub>2</sub>  $\xrightarrow{CO, 700^{\circ}C}$  Fe
  - (3) Fe  $\xrightarrow{\text{dil. H}_2\text{SO}_4}$  FeSO<sub>4</sub>  $\xrightarrow{\text{H}_2\text{SO}_4,\text{O}_2}$  Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>  $\xrightarrow{\text{heat}}$  Fe
  - (4) Fe  $\xrightarrow{O_2$ , heat FeO  $\xrightarrow{\text{dil. H}_2SO_4}$  FeSO<sub>4</sub>  $\xrightarrow{\text{heat}}$  Fe

(JEE Advanced 2014)

#### **Multiple Correct Answers Type**

- 1. Extraction of metal from the ore cassiterite involves
  - (1) Carbon reduction of an oxide ore
  - (2) Self-reduction of sulphide ore
  - (3) Removal of copper impurity
  - (4) Removal of iron impurity

(IIT-JEE 2011)

- The carbon-based reduction method is NOT used for the extraction of
  - (1) Tin from SnO,
  - (2) Iron from Fe<sub>2</sub>O<sub>3</sub>
  - (3) Aluminium from Al<sub>2</sub>O<sub>3</sub>
  - (4) Magnesium from MgCO<sub>3</sub>·CaCO<sub>3</sub>

(JEE Advanced 2013)

- 3. Upon heating with Cu<sub>2</sub>S, the reagent(s) that give copper metal is/are
  - (1) CuFeS,

(2) CuO

(3) Cu<sub>2</sub>O

(4) CuSO<sub>4</sub>

#### (JEE Advanced 2014)

- **4.** Copper is purified by electrolytic refining of blister copper. The correct statement(s) about this process is (are)
  - (1) Impure Cu strip is used as cathode
  - (2) Acidified aqueous CuSO<sub>4</sub> is used as electrolyte
  - (3) Pure Cu deposits at cathode
- (4) Impurities settle as anode-mud

(JEE Advanced 2015)

- 5. Extraction of copper from copper pyrite (CuFeS<sub>2</sub>) involves
  - (1) crushing followed by concentration of the ore by froth-flotation
- (2) removal of iron as slag
- (3) self-reduction step to produce 'blister copper' following evolution of  ${\rm SO}_2$
- (4) refining of 'blister copper' by carbon reduction

(JEE Advanced 2016)

# **Linked Comprehension Type**

#### Problems 1-3

Copper is the most noble of the first row transition elements. It occurs in small deposits in several countries. Ores of copper include chalcanthite (CuSO<sub>4</sub>·5H<sub>2</sub>O), atacamite [Cu<sub>2</sub>Cl(OH)<sub>3</sub>], cuprite (Cu<sub>2</sub>O), copper glance (Cu<sub>2</sub>S), and malachite [Cu<sub>2</sub>(OH)<sub>2</sub>CO<sub>3</sub>]. However, 80% of the world copper production comes from the ore chalcopyrite (CuFeS<sub>2</sub>). Extraction of copper from chalcopyrite includes roasting, iron removal, and self-reduction.

- 1. Partial roasting of chalcopyrite produces
  - (1) Cu<sub>2</sub>S and FeO

(2) Cu<sub>2</sub>O and FeO

(3) CuS and Fe<sub>2</sub>O<sub>3</sub>

(4) Cu<sub>2</sub>O and Fe<sub>2</sub>O<sub>3</sub>

- 2. Iron is removed from chalcopyrite as
  - (1) FeO

(2) FeS

 $(3) \text{ Fe}_2O_3$ 

- (4) FeSiO<sub>3</sub>
- 3. In self-reduction, the reducing species is
  - (1) S

(2)  $O^{2-}$ 

 $(3) S^{2}$ 

(4) SO<sub>2</sub>

(IIT-JEE 2010)

#### **Matrix Match Type**

 Match the extraction processes listed in Column 1 with the metals listed in Column II.

Ur.	Column I		Column II	
a.	Self-reduction	p.	Lead	
b.	Carbon reduction	q.	Silver	
c.	Complex formation and displacement by metal	r.	Соррет	
d.	Decomposition of iodide	s.	Boron	

(IIT-JEE 2006)

2. Match the conversions in Column I with the type(s) of reaction(s) given in Column II.

	Column I		Column II
a.	PbS → PbO	p.	Roasting
b.	$CaCO_3 \longrightarrow CaO$	q.	Calcination
c.	$ZnS \longrightarrow Zn$	r.	Carbon reduction
d.	$Cu_2S \longrightarrow Cu$	s.	Self-reduction

(IIT-JEE 2008)

3. Match the anionic species given in Column I that are present in the ore(s) given in Column II.

	Column I		Column II
1.	Carbonate	p.	Siderite
),	Sulphide	q.	Malachite
2.	Hydroxide	r.	Bauxite
ı.	Oxide	s.	Calamine
	- 137	t.	Argentite

(JEE Advanced 2015)

# **Numerical Value Type**

1. Galena (an ore) is partially oxidized by passing air through it at high temperature. After some time, the passage of air is stopped, but the heating is continued in a closed furnace such that the contents undergo self-reduction. The weight (in kg) of Pb produced per kg of O<sub>2</sub> consumed is \_\_\_\_\_\_

(JEE Advanced 2018)

# **Answers Key**

EXERC	ISES
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Single Cor	rect Answer	Туре		
<b>1.</b> (1)	<b>2.</b> (3)	<b>3.</b> (2)	<b>4.</b> (3)	<b>5.</b> (1)
<b>6.</b> (2)	<b>7.</b> (1)	<b>8.</b> (1)	<b>9.</b> (3)	10. (4)
<b>11.</b> (1)	<b>12.</b> (4)	<b>13.</b> (3)	<b>14.</b> (3)	<b>15.</b> (2)
<b>16.</b> (1)	<b>17.</b> (3)	<b>18.</b> (2)	<b>19.</b> (3)	<b>20.</b> (1)
<b>21.</b> (1)	<b>22.</b> (4)	<b>23.</b> (2)	<b>24.</b> (2)	<b>25.</b> (4)
<b>26.</b> (3)	<b>27.</b> (2)	<b>28.</b> (3)	<b>29.</b> (1)	<b>30.</b> (2)
<b>31.</b> (4)	<b>32.</b> (2)	<b>33.</b> (3)	<b>34.</b> (3)	<b>35.</b> (4)
<b>36.</b> (2)	<b>37.</b> (2)	<b>38.</b> (3)	<b>39.</b> (4)	<b>40.</b> (2)
41. (4)	<b>42.</b> (1)	<b>43.</b> (1)	<b>44.</b> (2)	<b>45.</b> (2)
<b>46.</b> (2)	<b>47.</b> (2)	<b>48.</b> (2)	<b>49.</b> (4)	<b>50.</b> (2)
<b>51.</b> (4)	<b>52.</b> (3)	<b>53.</b> (1)	<b>54.</b> (4)	<b>55.</b> (4)
<b>56.</b> (4)	<b>57.</b> (1)	<b>58.</b> (4)	<b>59.</b> (4)	<b>60.</b> (3)
<b>61.</b> (2)	<b>62.</b> (1)	<b>63.</b> (1)	<b>64.</b> (3)	<b>65.</b> (3)
<b>66.</b> (1)	<b>67.</b> (1)	<b>68.</b> (3)	<b>69.</b> (4)	<b>70.</b> (4)
<b>71.</b> (3)	<b>72.</b> (2)	<b>73.</b> (1)	<b>74.</b> (2)	<b>75.</b> (1)
<b>76.</b> (2)	<b>77.</b> (2)	<b>78.</b> (2)	<b>79.</b> (1)	<b>80.</b> (2)
<b>81.</b> (2)	<b>82.</b> (3)	<b>83.</b> (1)	<b>84.</b> (1)	<b>85.</b> (1)
<b>86.</b> (3)	<b>87.</b> (4)	<b>88.</b> (2)	<b>89.</b> (3)	<b>90.</b> (1)
<b>91.</b> (1)	<b>92.</b> (4)	<b>93.</b> (4)	<b>94.</b> (2)	<b>95.</b> (3)
<b>96.</b> (1)	<b>97.</b> (1)	<b>98.</b> (1)	<b>99.</b> (3)	<b>100.</b> (1)
<b>101.</b> (1)	<b>102.</b> (1)	<b>103.</b> (4)	<b>104.</b> (1)	<b>105.</b> (3)
<b>106.</b> (1)	<b>107.</b> (3)	<b>108.</b> (1)	<b>109.</b> (4)	<b>110.</b> (2)
111. (4)	<b>112.</b> (2)	<b>113.</b> (4)	<b>114.</b> (4)	<b>115.</b> (3)
<b>116.</b> (2)	<b>117.</b> (2)	<b>118.</b> (1)	<b>119.</b> (2)	<b>120.</b> (1)
<b>121.</b> (1)	<b>122.</b> (2)	<b>123.</b> (2)	<b>124.</b> (2)	<b>125.</b> (2)
<b>126.</b> (3)	<b>127.</b> (3)	<b>128.</b> (1)	<b>129.</b> (3)	<b>130.</b> (1)
131. (4)	<b>132.</b> (1)	133. (4)	134. (2)	<b>135.</b> (4)
136. (4)	<b>137.</b> (3)	<b>138.</b> (3)	<b>139.</b> (2)	<b>140.</b> (2)

# **142.** (1)

**141.** (4)

**143.** (3)

55.	(1, 4)
<b>58.</b>	(1, 2, 4)

**56.** (1, 2, 4) **59.** (2, 3)

57. (1, 4) **60.** (1, 4)

#### **Linked Comprehension Type**

<b>1.</b> (1)	<b>2.</b> (4)	<b>3.</b> (3)	<b>4.</b> (1)	<b>5.</b> (1)
<b>6.</b> (3)	<b>7.</b> (1)	<b>8.</b> (2)	9. (4)	10. (2)
<b>11.</b> (1)	<b>12.</b> (4)	<b>13.</b> (1)	14. (3)	<b>15.</b> (2)
<b>16.</b> (2)	<b>17.</b> (1)	<b>18.</b> (3)	<b>19.</b> (1)	<b>20.</b> (3)
<b>21.</b> (3)	<b>22.</b> (3)	<b>23.</b> (1)	<b>24.</b> (1)	<b>25.</b> (2)
<b>26.</b> (1)	<b>27.</b> (1)	<b>28.</b> (1)	<b>29.</b> (2, 3)	<b>30.</b> (1)
<b>31.</b> (3)	<b>32.</b> (2)	33. (2)	<b>34.</b> (3)	<b>35.</b> (2)
<b>36.</b> (1)	<b>37.</b> (1)	<b>38.</b> (1)	<b>39.</b> (2)	<b>40.</b> (1)
<b>41.</b> (1)	42. (2)	(-)	27. (2)	70.(1)

#### **Matrix Match Type**

Q. No.	a	b	c	d	e	f
1.	iv	iv	i, ii	ii	vi	v
2.	ii	ii, iii	i	v	iv	vi
3.	v	ii	iii	i	iv	vi
4.	vi	v	i	ii	vi	iii
5.	ii	iv	i	vi	v	iii
6	iii	i	ii	vi	iv	v
7	iv	i	v	iii	vi	ii
8.	iv	v	i	ii	vi	iii
9.	iii-q	i-r	ii-s	iv-p		

**10.** (1)

**11.** (3)

**12.** (2)

**13.** (4)

#### **Numerical Value Type**

1.(2)	<b>2.</b> (3)	<b>3.</b> (3)	<b>4.</b> (2)	<b>5.</b> (8)
<b>6.</b> (3)	7. (2)	<b>8.</b> (3)	<b>9.</b> (4)	<b>10.</b> (6)
11. (2)	<b>12.</b> (3)	<b>13.</b> (3)	<b>14.</b> (4)	<b>15.</b> (3)
16. (4)	17.(2)	<b>18.</b> (4)	<b>19.</b> (3)	<b>20.</b> (3)
<b>21.</b> (2)	22. (4)	<b>23.</b> (4)	<b>24.</b> (2)	<b>25.</b> (2)
26. (4)	<b>27.</b> (3)			

#### **ARCHIVES**

#### **JEE Main**

# **Single Correct Answer Type**

	- /->	2 (1)	4. (4)	<b>5.</b> (4)
<b>1.</b> (1)	<b>2.</b> (3)	<b>3.</b> (1)	4. (4)	3. (4)
<b>6.</b> (2)				

# **JEE Advanced**

# **Single Correct Answer Type**

<b>1.</b> (4) <b>2.</b> (1) <b>3.</b>	(2)
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#### **Multiple Correct Answers Type**

- **1.** (1, 4)
- **2.** (3, 4)
- **3.** (3)

- **4.** (2, 3, 4)
- **5.** (1, 2, 3)

#### **Linked Comprehension Type**

- **1.**(1)
- **2.** (4)
- **3.** (3)

#### **Matrix Match Type**

- 1. (a.  $\rightarrow$  p., r.; b.  $\rightarrow$  p.; c.  $\rightarrow$  q.; d.  $\rightarrow$  s.)
- 2.  $(a. \rightarrow p.; b. \rightarrow q.; c. \rightarrow p., r.; d. \rightarrow p., s.)$
- 3. (a.  $\rightarrow$  p., q., s.; b.  $\rightarrow$  t.; c.  $\rightarrow$  q., r.; d.  $\rightarrow$  r.)

#### **Numerical Value Type**

1.6.74 kg

# p-Block Group 15 Elements The Nitrogen Family

#### **OVERVIEW**

- 1. Group 15 elements of the periodic table are collectively known as pnicogens.
- 2. The general electronic configuration of elements of group 15 is  $ns^2 np^3$ .
- 3. Gradation in atomic and physical properties
  - a. Covalent radii:  $N < P < A_S < Sb < Bi$
  - b. Ionisation energy (IE):  $N > P > A_S > Sb > Bi$
  - c. Electronegativity (EN):  $N > P > A_S > Sb > Bi$
  - d. Melting point/K: N < P < Bi < Sb < As
  - e. Boiling point/K:  $P < N < A_S < B_i < Sb$
  - **f. Density:**  $N < P < A_S < Sb < Bi$
- **4.** Nitrogen exists as a diatomic inert gas whereas others exist in tetrahedra tetraatomic forms P<sub>4</sub>, As<sub>4</sub>, Sb<sub>4</sub> and are solids.
- 5. Metallic nature increases down the group.

Non-metals P As Sb Bi Metalloids Meta

- 6. Due to inert pair effect, group 15 elements show variable oxidation states of -3, +3 and +5. Stability of +5 oxidation state decreases down the group. Nitrogen besides -3, +3 and +5 oxidation states, also shows -2, -1, 0, +1, +2 and +4 oxidation states in its oxides.
- 7. Nitrogen shows maximum covalency of 4, whereas others can expand their covalency to 5 or 6 due to the presence of vacant *d*-orbitals in their valence shell.
- 8. Only nitrogen is capable of forming  $p\pi-p\pi$  multiple bonds with itself and with carbon, oxygen etc. due to compatibility in size and high extent of overlap of orbitals. Phosphorous and other members do not form  $p\pi-p\pi$  multiple bond but are capable of forming  $p\pi-d\pi$  bond.
- 9. Group 15 elements form hydrides of type, EH<sub>3</sub>

  Bond angle: NH<sub>3</sub> > PH<sub>3</sub> > AsH<sub>3</sub> > SbH<sub>3</sub> > BiH<sub>3</sub>

  Acidic character: NH<sub>3</sub> < PH<sub>3</sub> < AsH<sub>3</sub> < SbH<sub>3</sub> < BiH<sub>3</sub>

  Reducing agent: NH<sub>3</sub> < PH<sub>3</sub> < AsH<sub>3</sub> < SbH<sub>3</sub> < BiH<sub>3</sub>
- 10. a. Oxides of type  $X_2O_3$ ,  $X_2O_4$  and  $X_2O_5$  are formed by the elements of group 15.
  - **b.** Greater is the electronegativity more is the acidic nature of its oxides.
  - c. Acidic nature of each type decreases from N to Bi.

N<sub>2</sub>O<sub>3</sub> P<sub>2</sub>O<sub>3</sub> As<sub>2</sub>O<sub>3</sub> Sb<sub>2</sub>O<sub>3</sub> Bi<sub>2</sub>O<sub>3</sub>
Amphoteric Basic

However, it shows feeble acidic character with strong alkali.

N<sub>2</sub>O<sub>5</sub>, P<sub>2</sub>O<sub>5</sub>, As<sub>2</sub>O<sub>5</sub>, Sb<sub>2</sub>O<sub>5</sub>, Bi<sub>2</sub>O<sub>3</sub>
Acidic nature decreases

- Acidic nature of  $M_2O_4$  oxides also decreases from  $N_2O_4$  to  $Bi_2O_4$ .
- d. Thermal stability decreases in each series from N to Bi.
- **e.** In the oxides of a particular element, the acidic nature increases as the percentage of oxygen increases or the oxidation state increases.
- 11. All the members of group 15 form oxyacids or oxoacids. The strength and stability of oxoacids having the element in same oxidation state decreases down the group.
- 12. Except nitrogen, the rest of the elements of group 15 form two series of halides ECl<sub>3</sub> and ECl<sub>5</sub>. Nitrogen does not form pentahalides due to absence of *d*-orbitals in its valence shell.
- **13.** With the exception of N, all other group 15 elements form sulphides.
- **14.** For drying NH<sub>3</sub>, quicklime (CaO) is used. Other dehydrating agents like H<sub>2</sub>SO<sub>4</sub>, CaCl<sub>2</sub>, P<sub>2</sub>O<sub>5</sub> cannot be used as they react with NH<sub>3</sub>.
- 15. Nitrogen forms five oxides:

N<sub>2</sub>O, NO, N<sub>2</sub>O<sub>3</sub>, NO<sub>2</sub> or N<sub>2</sub>O<sub>4</sub> and N<sub>2</sub>O<sub>5</sub>

- **16.** HNO<sub>3</sub> also known as **aqua fortis** (meaning strong water) acts as monobasic acid. Noble metals like Au, Pt etc. dissolve in aqua regia i.e. [3HCl (conc.) + 1 HNO<sub>3</sub>(conc.)]
- 17. Proteins react with HNO<sub>3</sub> to form a yellow compound called xanthoprotein.
- **18.** HNO<sub>3</sub> is used in manufacturing of explosives like TNT, picric acid, nitroglycerine etc.
- 19. Phosphoric exists in number of allotropic forms. Important ones are white or yellow phosphorous, red phosphorous and black phosphorous. White phosphorous is the most reactive allotrope.
- **20.** Persons working with phosphorous develop a disease known as **phossy jaw**.
- 21. Some of the important compounds of group 15 are as follows:

i. Scheele's green CuHAsO<sub>3</sub>ii. Graham salt (NaPO<sub>3</sub>)<sub>6</sub>

iii. Paris green (CH<sub>3</sub>COO)<sub>2</sub>Cu.3Cu(AsO<sub>2</sub>)<sub>2</sub>

iv. Pearl white BiOCl

v. Nitrophosphate  $Ca(H_2PO_2)_2 + 2Ca(NO_3)_2$ 

vi. Superphosphate of lime  $Ca(H_2PO_4)_2H_2O +$ 

2CaSO<sub>4</sub>·2H<sub>2</sub>O

vii. Thomas slag

2Ca<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>CaSiO<sub>3</sub>

viii.Sindri fertilizer

ix. Nangal fertilizer (CAN) Ca(NO<sub>3</sub>), NH<sub>4</sub>NO<sub>3</sub>

Amatol 80% NH<sub>4</sub>NO<sub>3</sub> + 20% T.N.T.

xi. Ammonal NH, NO, + Al powder

(small quantity)

 $(NH_{4}),SO_{4}$ 

xii. Swarts reagent SbF,

xiii. Tartaremetic (Potassium antimonyl tartarate)

xiv. Angelis salt Na,N,O,·H,O

22. a. Radioactive phosphorous (32P) is used in the treatment of leukemia.

**b.** In toothpaste, CaHPO<sub>4</sub>·2H,O is added as a mild abrasive and polishing agent.

c. Amatol is 80% NH<sub>4</sub>NO<sub>3</sub> + 20% TNT and is used as an explosive.

d. P<sub>4</sub>S<sub>3</sub> is used in matches. The head of the safety match box contains KClO<sub>3</sub>, KNO<sub>2</sub> or red lead along with grounded glass pieces and antimony sulphide. Sides of match box contain red phosphorous and sand powder

23. Some examples of hybridisation of group 15 (5e<sup>©</sup>)

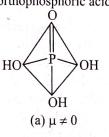
Symbols used: SN = Steric number, lp = lone pair, bp =  $b_{0nd}$ pair, H = hybridisation, G = Geometry, S = Shape, T.H. Tetrahedron, Tbp = Trigonal bipyramid, O.H. = Octahedral Pbp = Pentagonal bipyramid, T.E. = Transition elements C.N. Coordination number, V = No. of valence  $e^{-s}$ ,  $M = N_{0.0}$ monovalent atom attached to central atom, O.S. =  $Oxidati_{0h}$ state, (e) = equatorial bond, (a) = axial bond.

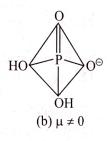
Note: Oxoacids and peroxoacids and their ions have same hybridisation, geometry and shape.

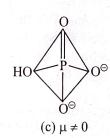
#### **OXOACIDS OF PHOSPHOROUS**

1. H,PO, (Tribasic acid) (O.S. = +5)(Phosphoric acid) or (orthophosphoric acid) H,PO,⊖ (Dihydrogen phosphate ion)

HPO,2-(Hydrogen phosphate) PO,3-(Phosphate ion) [One  $(p\pi-d\pi)$  multiple bond]







Due to four equivalent resonance structures

(P — O) Bond order = 1.5  

$$H = \frac{1}{2}(V+M) = \frac{1}{2}(5+3) = 4$$

$$SN = 4 bp$$

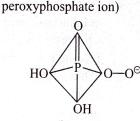
H,PO,⊖

(Dihydrogen-

 $H = sp^3$ 

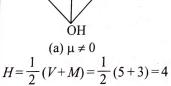
Geometry = T.H.,  $109^{\circ}$ ,  $28^{\circ}$ 

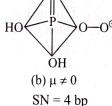
2.  $H_3PO_5$  (O.S. = +5) (Peroxyphosphoric acid) or (Perphosphoric acid)



HPO,2-(Hydrogen-peroxy phosphate ion)

PO.3-(Peroxyphosphate ion) [One  $(p\pi-d\pi)$  multiple bond]





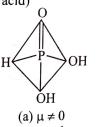
HO
$$\begin{array}{c}
O \\
O \\
O \\
O \\
O \\
H = sp^{3}
\end{array}$$

Geometry = T.H., 
$$109^{\circ}$$
,  $28$ 

3. H<sub>3</sub>PO<sub>3</sub> (Dibasic acid) (O.S. = +3)

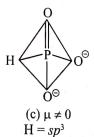
H,PO,<sup>⊖</sup> (Dihydrogen phosphite ion) HPO,2-(Hydrogen phosphite ion) [One  $(p\pi-d\pi)$  multiple bond]

(Phosphorous acid) or (Phosphoric acid)

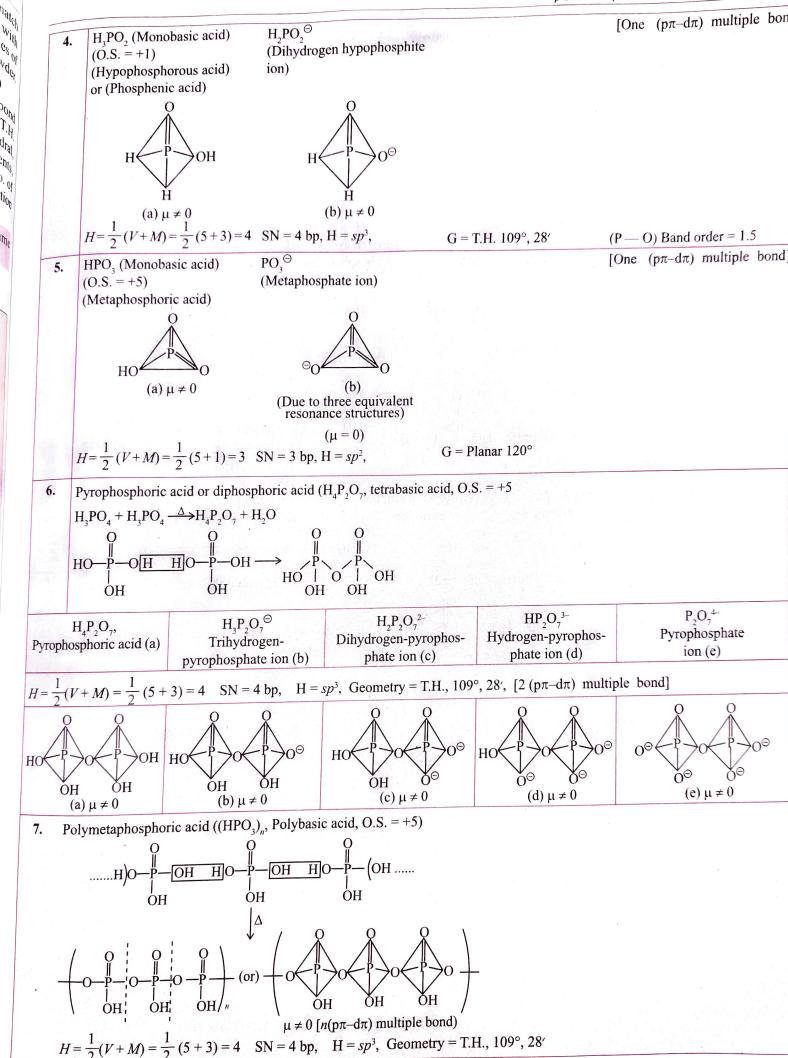


(P - O) Bond order = 1.5

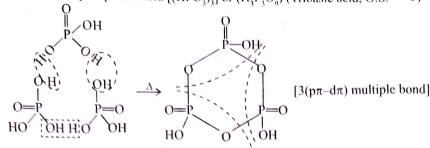
H
P
OH
(b) 
$$\mu \neq 0$$
SN = 4 bp



Geometry = T.H.,  $109^{\circ}$ ,  $28^{\circ}$ 



8. Cyclotrimeta phosphoric acid  $[(HPO_3)_3]$  or  $(H_3P_3O_9)$  (Tribasic acid, O.S. = +5)



H,P,O., Cyclotrimetaphosphoric acid

H,P,O,O Dihydrogencyclotrimeta phosphate ion

phosphate ion

HP<sub>3</sub>O<sub>9</sub><sup>2-</sup> P<sub>3</sub>O<sub>9</sub><sup>3-</sup>
Hydrogen cyclotrimeta- Cyclotrimeta phosphate

 $H = \frac{1}{2}(V + M) = \frac{1}{2}(5 + 3) = 4$ 

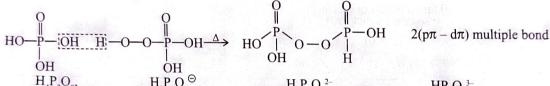
SN = 4 bp

 $H = sp^3$ ,

Geometry = T.H.,  $109^\circ$ , 28'

9. Perdiphosphoric acid (H<sub>4</sub>P<sub>2</sub>O<sub>8</sub>), Tetrabasic, O.S. = +5)

$$H_3PO_4 + H_3PO_5 \xrightarrow{\Delta} H_4P_2O_8 + H_2O$$



Perdiphosphoric Trihydrogenperdiphosphate ion

 ${
m H_2P_2O_8^{\ 2-}}$ Dihydrogen perdiphos-

HP,O,3-Hydrogen peridiphosphate ion

Perdiphosphate ion

$$H = \frac{1}{2}(V + M) = \frac{1}{2}(5 + 3) = 4$$
 SN = 4 bp,

phate ion

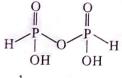
 $H = sp^3$ ,

Geometry = T.H.,  $109^{\circ}$ , 28'

10. Pyrophosphrous acid (H<sub>4</sub>P<sub>2</sub>O<sub>5</sub>)

(Dibasic, O.S. = +3)

 $2(p\pi - d\pi)$  multiple bond



 $H = \frac{1}{2}(V + M) = (5 + 3) = 4$  SN = 4.bp,

 $H_3P_2O_5^{\Theta}$ Trihydropyro-

phosphite ion

H,P,O<sub>5</sub><sup>2-</sup> Dihydropyrophosphite ion

 $H = sp^3$ 

 $H = sp^3$ 

Geometry =  $T.H_{*}$ .

11. Hypophosphoric acid (H<sub>4</sub>P<sub>2</sub>O<sub>6</sub>) (Tetrabasic, O.S. = +4)

 $2(p\pi - d\pi)$  multiple bond

OH OH  $H = \frac{1}{2} (V + M) = (5 + 3) = 4$ (P - O) bond order = 1.5

SN = 4 bp

SN = 3 bp

 $H_3P_2O_6^{\ \Theta}$   $H_2P_2O_6^{\ 2-}$  Trihydrohypo- Dihydrohypophosphate ion phosphate ion

HP<sub>2</sub>O<sub>6</sub><sup>3-</sup> HydrohypoHypophosphate ion

phosphate ion

Geometry = T.H.

12.  $HNO_3$  (nitric acid, monobasic, O.S. = +5)

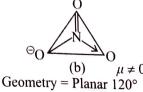
NO,<sup>⊙</sup> nitrate ion

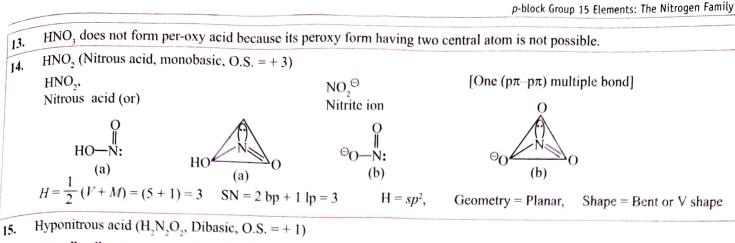
N atom does not have *d*-orbitals. So [one  $(p\pi-p\pi)$  multiple bond]

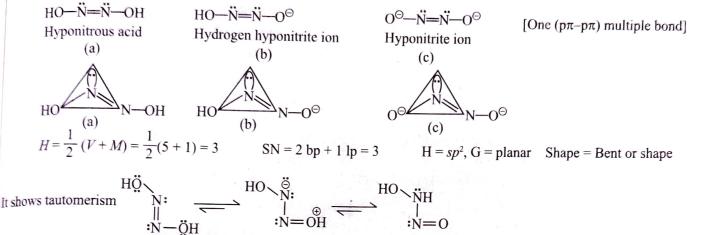
$$\begin{array}{c} O \\ \parallel \\ HO - N: \rightarrow O \\ (a) \end{array}$$

 $H = \frac{1}{2}(V + M) = (5 + 1) = 3$ 

 $H = sp^2$ 







# 24. Oxides of Nitrogen and their ions:

S. No.	Oxides of nitrogen and O.S. of N	Characteristics	SN	Hyb. (H)	Geometry and shape, (G and S) and dipole moment
1.	Nitrous oxide or laughing gas $(N_2O) (O.S. = +1)$ $: N^a = N^{:b} \longrightarrow O^{:c}$ or $: N^a = N^{:b} \longrightarrow O^{:c}$ one bond pair	Neutral and diamagnetic $2(p\pi-p\pi)$ multiple bonds	SN at $N^a = 1$ bp + 1 lp = 2 SN at $N^b = 2$ bp = 2	sp	G = Linear μ≠0
	Nitric oxide  N=0  O.S. = +2)	Neutral and paramagnetic $(p\pi-p\pi)$ multiple bonds	$SN = 1 \text{ bp} + 1 \text{ lp} + 1 \text{ odd}$ electrons = 3 $H = \frac{1}{2} (V + M + \text{ odd}$ electrons) $= \frac{1}{2} (5 + 0 + 1) = 3$	sp <sup>2</sup>	$G = Planar$ $Shape = Linear$ $\begin{pmatrix} \ddots \\ N \\ \downarrow \end{pmatrix}$ $\mu \neq 0$
0	2 3'	Acidic and diamagnetic 2(pπ–pπ) multiple bonds	SN at N <sup>a</sup> = 3 bp SN at N <sup>b</sup> = 2 bp + 11p = 3 $H = \frac{1}{2} (V + M)$ rule is not applicable in this case.	$sp^2$	G at $N^a$ = Planar G at $N^b$ = Planar Shape at $N^b$ = Bent $\mu \neq 0$

	Thorganic chemistry				
4.	Nitrogen dioxide (NO <sub>2</sub> ) (O.S. = +4) O $\leftarrow$ N=O (OR) $\ominus$ $\rightarrow$ N=O	Acidic and paramagnetic one $(p\pi-p\pi)$ multiple bonds	$SN = 2bp + 1 \text{ odd electron} = 3.$ $H = \frac{1}{2}(V+M) + 1 \text{ odd electron}$ $= \frac{1}{2}(5+0+1) = 3)$	$sp^2$	G = Planar, Shape = Bent $\mu \neq 0$ O $O$ $O$ $O$ $O$ $O$ $O$ $O$ $O$ $O$
5.	Dinitrogen tetraoxide $(N_2O_4)$ (O.S. = +4) $O=N^{(a)}-N^{(b)}=O$ $\downarrow$ $\downarrow$ $(OR)$ O=N-N=O $\downarrow$ $\downarrow$ $\downarrow$ $\downarrow$ $\downarrow$ $\downarrow$ $\downarrow$ $\downarrow$ $\downarrow$ $\downarrow$	Acidic and diamagnetic 2(pπ–pπ) multiple bonds	Same SN at N <sup>a</sup> or N <sup>b</sup> . SN = 3 bp = 3 $H = \frac{1}{2} [(V + M \pm \text{charge})]$ rule is not applicable in this case.	$sp^2$	$G = Planar$ $\mu \neq 0$
6.	Dinitrogen pentaoxide $(N_2O_5)$ (O.S. = +5) $O=N^{(a)}-O-N^{(b)}=O$ O O O O O O O	Acidic and anhydride of HNO <sub>3</sub> , i.e. $O=N^{(a)}-OH-HO-N=O$ $O=N-O-N=O$ $O=(D\pi-p\pi)$ multiple bond	Same SN at N <sup>a</sup> or N <sup>b</sup> . SN = 3 bp = 3 $H = \frac{1}{2} [(V + M \pm \text{charge})]$ rule is not applicable in this case.	$sp^2$	G = Planar μ≠0
7.	$NO_2^{\oplus}(O.S. = +5)$ $\vdots \ddot{O} = N = \ddot{O}$ : 2 bond pairs ( $\pi$ bonds are excluded from hybridisation)	Acidic and diamagnetic 2 (pπ–pπ) multiple bond	SN = 2 bp = 2 $H = \frac{1}{2} [V + M - (+\text{ve charge})]$ $= \frac{1}{2} (5 + 0 - 1) = 2$	sp	$G = Planar$ Bond angle = $180^{\circ}$ $\mu = 0$
8.	$NO_2^{\Theta}$ $(O.S. = +3)$ Nitrite ion $NO_2^{\Theta}$ $OOOOOOOOOOOOOOOOOOOOOOOOOOOOOOOOOOOO$	Acidic and diamagnetic one $(p\pi-p\pi)$ multiple bond	SN = 2  bp + 1  lp = 3 $H = \frac{1}{2}[V + M + \text{No. of -ve charge}]$ $= \frac{1}{2}(5 + 0 - 1) = 3$	$sp^2$	G = Planar Shape = Bent $\mu \neq 0$ Expected bond angle = 120° But observed bond angle = 115°
6	$NO_3^{\Theta}$ $(O.S. = +5)$ Nitrite ion $O=N-O^{\Theta}$ $O$		SN = 3  bp = 3 $H = \frac{1}{2}[V + M + \text{No. of -ve charge}]$ $= \frac{1}{2}(5 + 0 + 1) = 3$	$sp^2$	$G = Planar$ $\mu = 0$ Bond angle = $120^{\circ}$
	(Azide ion)	The possible linear structures are  [:N=N=N:]  (a)  SN on the central N atom in all s	-N≡N:] <sup>⊙</sup> [:N≡N-(c)		near

# 2.1 INTRODUCTION

Group 15 of the periodic table comprises nitrogen (N), phosphorous (P), arsenic (As), antimony (Sb) and bismuth (Bi). These elements are collectively known as **pnicogen** and their compounds as oniconides. The name pnicogen is derived from the Greek word pnicomigs which means suffocation. Pniconides contain E<sup>3</sup>-species. These are p-block elements as the last differentiating element is accommodated in np orbitals

# 2.2 OCCURRENCE

Molecular nitrogen comprises 78% (by volume) of the earth atmosphere, but it is not very abundant in the earth crust. Nitrogen is the thirty-third most abundant element by mass in the earth crust. Nitrogen mainly occurs as nitrates i.e. chile saltpetre (NaNO<sub>3</sub>) and Indian saltpetre (KNO<sub>3</sub>). Nitrogen is an essential constituent of proteins and amino-acids. Nitrates and other nitrogen compounds are extensively used in fertilisers and explosives. phosphorous is the eleventh most abundant element in the earth crust. It is highly reactive and does not occur free in nature. It occurs in minerals of the apatite family, Cao(POA)cCaX, (X=F, Clor OH) i.e. fluorapatite, Ca<sub>9</sub>(PO<sub>4</sub>)<sub>6</sub>. CaF<sub>2</sub>, chloropatite, Ca<sub>0</sub>(PO<sub>4</sub>)<sub>6</sub>·CaCl<sub>2</sub> or hydroxyapatite, Ca<sub>0</sub>(PO<sub>4</sub>)<sub>6</sub>·Ca(OH)<sub>2</sub>. These are main components of phosphate rocks. Phosphorous is an essential constituent of animal and plant matter. It is present in bones as well as in living cells. Phosphoproteins are present in milk and eggs. It also occurs in nucleic acids, i.e. DNA and RNA which control the hereditary effects in human beings and in adenosine triphosphate (ATP) and adenosine diphosphate (ADP) which are of vital importance for the production of energy in cells.

The elements As, Sb and Bi are not very abundant. Their most important source is as sulphides occurring as traces in other ores. The only common ores of arsenic are:

1. Arsenopyrites - FeAsS

As<sub>4</sub>S<sub>4</sub>As<sub>2</sub>S<sub>3</sub> 2. Realgar

3. Orpiment

The most important ore of antimony is stibnite, Sb,S,. Bismuth occurs as bismuthinite (Bi<sub>2</sub>S<sub>3</sub>) and bismite (Bi<sub>2</sub>O<sub>3</sub>).

# 2.3 ATOMIC AND PHYSICAL PROPERTIES

Some of the important atomic and physical properties of group 15 elements along with their electronic configurations are given in Table 2.1.

#### 2.3.1 ELECTRONIC CONFIGURATION

The general valence shell electronic configuration of group 15 is  $ns^2np^3$  (where n=2 to 6). The three electrons in the np orbitals are distributed as  $np_{v}^{-1}np_{v}^{-1}np_{v}^{-1}$  in accordance with Hund's rule.

The ns orbital in group 15 elements is completely filled and np orbitals are half filled, making their electronic configuration extra stable.

#### 2.3.2 ATOMIC AND IONIC RADII

1. Down the group  $(\downarrow)$ , i.e. from N to Bi, the covalent (atomic) and ionic radii (in a particular oxidation state) increases. There is considerable increase in covalent radius from N to P. However, from As to Bi only a small increase in covalent radius is observed.

**Explanation:** Down the group  $(\downarrow)$ , i.e. from N to Bi, with addition of a new principal energy shell in each succeeding element, effective nuclear charge decreases and covalent radii increases. But the increase in radii at each step is not the same due to difference in electronic configuration of N and P on one hand and As, Sb and Bi on other hand. In N and P, the valence shell electrons are preceded by noble gas core, hence shielding effect is very high and thus decrease in effective nuclear charge is high and there is considerable increase in radii from N to P. But in As, Sb and Bi, in between the valence shell electrons and noble gas core lesser shielding fully filled d and/or f orbitals are present. Thus shielding effect is less and effective nuclear charge increases which reduces the effect of addition of a new energy shell to some extent. Hence from As to Bi, increase in covalent radii is very less.

Table 2.1 Atomic and physical properties of Group 15 element

Table 2.1 Atomic and physical pro	Nitrogen	Phosphorous	Arsenic	Antimony	Bismuth
	N. (12.2.2.2.2.1.1.1.1.1.1.1.1.1.1.1.1.1.1.	Р	As	Sb	Bi
Symbol	N	15	33	51	83
Atomic number	7	30.97	74.92	121.75	208.98
Atomic mass/(g mol <sup>-1</sup> )	14.01	[Ne] $3s^23p^3$	[Ar] $3d^{10}4s^24p^3$	[Kr] $4d^{10}5s^25p^3$	[Xe] $4f^{14}5d^{10}6s^26p^3$
Electronic configuration  onisation enthalpy/(kJ mol <sup>-1</sup> ) I  II	[He] 2s <sup>2</sup> 2p <sup>3</sup> 1402 2856 4577	1012 1798 2910	947 1798 2736	834 1595 2443	703 1610 2466 1.9
Electronegativity  Covalent radius/(pm) <sup>a</sup>	3.0	2.1	2.0 121 222 <sup>b</sup>	1.9 141 76°	1.9 148 103°
onic radius/(pm)	171	$\frac{212^{b}}{317^{e}}$	1089	904	544
Melting point / (K)	63 <sup>d</sup>	554 <sup>e</sup>	888g	1860 6.697	1837 9.808
Boiling point/(K) Density at 298 K/(g cm <sup>-3</sup> )	0.879	1.823	5.778i	0.097	

"E" single bond (E = element);  ${}^{b}E^{3-}$ ; C  $E^{3+}$ ; "Molecular nitrogen; "white phosphorous;

Grey (α-form) at 38.6 atm; sublimation temperature; hat 63 K; Grey α-form.

**2.** The atomic radii of elements of group 15 are less than the corresponding elements of group 14.

**Explanation:** From left to right  $(\rightarrow)$  i.e. from group 14 to 15 in a given period, with increase in nuclear charge, the electron is added in the same shell. Consequently, the effective nuclear charge increases and covalent radii decreases.

e.g. atomic or covalent radii of N is less than carbon.

### 2.3.3 IONISATION ENTHALPY (IE or $\Delta$ , $H^{\odot}$ )

The ionisation enthalpies of the elements of group 15 are much higher than the corresponding elements of group 14. Down the group (\$\psi\$) the values of the ionisation energies decrease. **Explanation:** Because of increased nuclear charge, reduced atomic radii and stable half-filled configurations, they have much less tendency to lose electrons as they are more tightly held by the nucleus. Consequently the ionisation enthalpies of group 15 elements are much higher as compared to elements of group 14 carbon family. The decrease in their values, down the group is due to gradual increase in the atomic size which reduces the force of attraction on the electrons by the nucleus.

IE: N > P > As > Sb > Bi

#### 2.3.4 ELECTRONEGATIVITY (EN)

Group 15 elements are more electronegative than group 14 elements. Electronegativity of elements of group 15 shows a gradual decrease down the group from N to Bi.

**Explanation:** As the elements of group 15 have smaller atomic size and need less number of electrons to attain noble gas configuration as compared to elements of group 14, they are more electronegative. Down the group, due to the gradual increase in the atomic size, attraction by the nucleus for the electrons decreases. Hence their electronegativity values decrease down the group.

EN: N > P > As > Sb > Bi

#### 2.3.5 MELTING AND BOILING POINTS

The melting points of group 15 elements first increase from nitrogen to arsenic and then decrease to antimony and bismuth. The melting points of antimony and bismuth are less than the expected values. The boiling points, however, increase regularly from N to Bi.

**Explanation:** The melting points increase down the group due to increase in their atomic size. The unexpected decrease in the melting points of antimony and bismuth is because of their tendency to form three covalent bonds instead of five covalent bonds due to **inert pair effect**. This results in weakening the attraction among their atoms thus lowering their melting points. Because of larger size of atoms, bismuth has still weaker interatomic forces than antimony and thus has lower melting points.

Melting points: N < P < Bi < Sb < As

Down the group  $(\downarrow)$ , i.e. from N to Bi, boiling points increase due to an increase in their atomic size (exception P < N).

Boiling points: P < N < As < Bi < Sb

#### 2.3.6 DENSITY

The density of the element of group 15 increases regularly from N to Bi as usual.

# 2.3.7 METALLIC CHARACTER

Metallic character increases down the group ( $\downarrow$ ) from N to Bi

**Explanation:** Down the group, the atomic size increases and the outer electrons get farther from the nucleus. The ionisation energy decreases and the electrons become more loosely held and have a tendency to be lost readily. Thus the metallic character increases. First two elements of this group (N and P) are non, metals, the next two (As and Sb) are metalloids, while Bi is a typical metal. Thus the metallic character increases from N to Bi

The elements of group 15 are less metallic than the corresponding elements of group 14. This is due to increase  $i\eta$  nuclear charge and electronegativity from group 14 to group 15 hence the metallic character decreases from group 14 to 15.

#### 2.3.8 ATOMIC AND PHYSICAL STATE

Nitrogen exists as diatomic gaseous molecule, phosphorous, arsenic and antimony exist as discrete tetrahedra tetraatomic solid molecules and bismuth is metallic at ordinary temperature.

#### 2.3.9 $p\pi - p\pi$ Multiple Bond

Nitrogen because of its small size and high electronegativity forms  $p\pi - p\pi$  multiple bonds with itself and with other elements having small size and high electronegativity (e.g., C, O). Thus, nitrogen exists as a diatomic molecule with a triple bond ( $N \equiv N$ , one  $\sigma$ - and two  $\pi$ - bonds) between the two atoms. These  $N_2$  molecules are held together by weak van der Waals forces of attraction which can be easily broken by the collisions of the molecules at room temperature. Therefore,  $N_2$  is a gas at room temperature. Since bond dissociation enthalpy (941.4 kJ mol) of  $N \equiv N$  molecule is very high.  $N_2$  is an inert gas.

The other elements of group 15 do not form  $p\pi$ – $p\pi$  multiple bonds since their atomic orbitals are large and diffused that they cannot have effective overlapping. Thus, P, As and Sb do not form  $p\pi$ – $p\pi$  multiple bonds. Instead they prefer to form single bonds as P—P. As—As and Sb—Sb while Bi forms metallic bonds in the elemental state. Actually, phosphorus, arsenic and antimony exist as discrete tetraatomic tetrahedral molecules such as  $P_4$  As $_4$ , Sb $_4$ , etc. containing E—E single bonds.

Due to bigger size, the forces of attraction holding the tetraatomic molecules of  $P_4$ ,  $As_4$ ,  $Sb_4$ , etc. are quite strong and hence cannot be broken by the collisions of the molecules at room temperature. Therefore,  $P_4$ ,  $As_4$ ,  $Sb_4$  all are solids at room temperature.

#### 2.3.10 CATENATION

The elements of group 15 also show the property of catenation (self-linking of atoms) but to a much smaller extent than elements of group 14. The reason being that the E—E bond strength of these elements is much lower than that of C—C bond.

Among the elements of group 15, phosphorus has the maximum tendency for catenation forming cyclic as well open chain compounds consisting of many phosphorus atoms.

Nitrogen has little tendency for catenation since N—N single bond is very weak due to large interelectronic repulsions between the lone pairs of electrons present on the N-atoms of N—N bond having small bond length. As a result the catenation tendency is weaker in nitrogen. Another factor which affects the chemistry of nitrogen is the absence of d orbitals in its valence shell. Besides restricting its covalency to four, nitrogen cannot form  $d\pi$ — $d\pi$  bond as the heavier elements can e.g.,  $R_3P = O$  or  $R_3P = CH_2$  (R = alkyl group). Phosphorus and arsenic can form  $d\pi$ — $d\pi$  bond also with transition metals when their compounds like  $P(C_2H_5)_3$  and  $As(C_6H_5)_3$  act as ligands.

Nitrogen can form chains containing up to three N-atoms, e.g., hydrazoic acid,  $N_3H$  or azide ion,  $N_3^{\odot}$  ion. Due to decrease in E—E bond strength down the group, catenating ability decreases from P to As. As can form a chain of only two atoms.

# 2.4 CHEMICAL PROPERTIES

#### 2.4.1 OXIDATION STATES

The elements of group 15 have  $ns^2$   $np^3$  as their valence shell electronic configuration. They can complete their octets in two different ways:

1. Electron transfer: The atoms of the elements of this group may accept three electrons from more metallic elements to form triply charged negative ions such as nitride, N<sup>3</sup>-ion and phosphide, P<sup>3</sup>-ion and thereby attain noble gas configuration. Only small atoms can form highly charged negative ions because of their greater electronegativities. Obviously nitrogen with greater electronegativity and smaller size, has a stronger tendency to form triply charged negative ions and this tendency decreases down the group because of increase of size and decrease in electronegativity.

The elements of this group also exhibit +3 and +5 oxidation states. The +5 ions are generally not known because their sizes will be very small and their ionisation energy will be very high. Down the group, the stability of +3 oxidation state increases while that of +5 decreases. This is due to **inert pair effect** as  $ns^2$  electrons tend to remain paired in heavier p-block elements i.e., they do not take part in the bond formation. It is due to the fact that s-electrons are penetrating in the preceding shell in such a way that they are a part of inner shell electrons and are, therefore, removed with difficulty.

 $Bi^{3+}$  and  $Sn^{3+}$  are stable due to decrease in IE.  $BiF_3$  is known, but  $BiF_5$  is not.

Besides -3, N and P also show oxidation states of -2 in hydrazine (NH<sub>2</sub>NH<sub>2</sub>) and diphosphine (PH<sub>2</sub>PH<sub>2</sub>) respectively. Nitrogen also shows an oxidation state -1 in hydroxylamine (NH<sub>2</sub>OH) but phosphorous does not. In case of nitrogen, all O.S. from +1 to +4 bend to disproportionate in acid solution. For example,

 $3HNO_2 \longrightarrow HNO_3 + H_2O + 2NO$ 

2. Electron sharing: Since the atoms of these elements contain three unpaired p-electrons so these can pair with unpaired electrons in another atom or atoms to form covalent bonds e.g., NH<sub>3</sub>, PH<sub>3</sub>, AsH<sub>3</sub>, SbH<sub>3</sub>, BiH<sub>3</sub>.

## 2.4.2 MAXIMUM COVALENCY

Since nitrogen does not possess any vacant d-orbitals in its valence shell (n=2), it, therefore, cannot extend its valency beyond four  $[NH_4^{\oplus}, NR_4^{\oplus}]$ . That is the reason why nitrogen does not form  $NF_5$  or  $NCl_5$ . On the other hand, phosphorous and other elements have empty d-orbitals and can utilise all their valence electrons to exhibit covalency of five or six, e.g.  $PCl_5$ ,  $[SbF_6]^{\odot}$   $AsF_5$ ,  $[PF_6]^{\odot}$ .

# 2.4.3 NATURE OF BONDING

In majority of the compounds of these elements the bonds are covalent. Nitrogen and phosphorous are predominantly covalent through they may form ionic nitrides and phosphides by accepting 3 electrons. The strength of the covalent bonding decreases down the group  $(\downarrow)$  i.e. covalent bonding strength is in the order:

 $N > P > A_S > Sb > Bi$ 

# 2.5 CHEMICAL REACTIVITY

# 2.5.1 REACTIVITY TOWARDS HYDROGEN —FORMATION OF HYDRIDE

All the elements of group 15 form volatile hydrides having formula  $EH_3$ , where E = N, P, As, Sb and Bi.

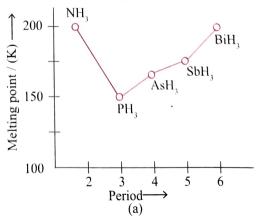
**Bond angle:** According to VSEPR theory, lone pair—bond pair (lp—bp) repulsion is greater than bond pair—bond pair (bp—bp) repulsion, this leads to contraction in the bond angle, i.e. bond angle is less than 109.28° (Tetrahedral angle). Consequently, all the group 15 hydrides have pyramidal shape. The bond angles are as follows:

NH<sub>3</sub> PH<sub>3</sub> AsH<sub>3</sub> SbH<sub>3</sub> BiH<sub>3</sub> 107.8° 93.6° 91.8° 91.3° 90°

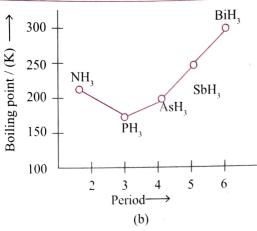
**Explanation:** The decrease in the bond angle can be explained on the basis of the size and electronegativity of the central atom. Due to small size and high electronegativity of N-atom, the electron density on N-atom is highest. So repulsions between the electron pairs is maximum and so is the bond angle. From N to Bi, size increases and electronegativity decreases. This results in decrease of electron density on the central atom. As a result, the repulsion between the electron pairs decreases and hence the bond angle also decreases.

#### 2.5.2 CHARACTERISTICS OF HYDRIDES

#### 1. Melting point and boiling point :



[Melting point:  $NH_3$  (195.2) >  $BiH_3$  ( $\approx$ 190) >  $SbH_3$  (185) >  $AsH_3$  (156.7) >  $PH_3$  (139.5) K]



[Boiling point: BiH<sub>3</sub> (290) > SbH<sub>3</sub> (254.6) > NH<sub>3</sub> (238.5) > AsH<sub>3</sub> (210.6) > PH<sub>4</sub> (185.5) K]

Fig. 2.1 (a) and (b) Melting and boiling points of hydrides of group 15

Explanation of hy	ydrides of group 15
Melting point	Boiling point
The melting point of NH <sub>3</sub> is highest in the hydrides of group 15 due to intermolecular H-bonding.  In this case increased molecular masses of BiH <sub>3</sub> and SbH <sub>3</sub> do not affect so much the melting point of NH <sub>3</sub> . Because the increased van der Waals forces are not so strong in the solid state as they are in liquid state.  OR  The H-bonding in NH <sub>3</sub> is stronger in the solid state than in the liquid or gaseous state.	BiH <sub>3</sub> and SbH <sub>3</sub> due to their high molecular mass as compared to that of NH <sub>3</sub> . The increased molecular masses of BiH <sub>3</sub> and SbH <sub>3</sub> increases the <b>van der</b> <b>Waals</b> forces of attraction in liquid state.

2. Thermal stability: The thermal stability of hydrides of the elements of group 15 decreases gradually from NH<sub>3</sub> to BiH<sub>3</sub>. SbH<sub>3</sub> and BiH<sub>3</sub> are thermally unstable whereas BiH<sub>3</sub> has been obtained in traces only.

Down the group  $(\downarrow)$  as the bond length (internuclear) distance between hydrogen and group 15 element increases, the bond strength E-H decreases and consequently thermal stability decreases.

Thermal stability:  $NH_3 > PH_3 > AsH_3 > SbH_3 \geq BiH_3$ 

3. Reducing agent: The reducing character of hydrides of group 15 elements increases down the group. Because of decrease in thermal stability from NH<sub>3</sub> to BiH<sub>3</sub>. The tendency to give hydrogen and act as reducing agent gradually increases from NH<sub>3</sub> to BiH<sub>3</sub>. The reducing character thus depends on the instability of the hydride. The greater the instability, greater is its reducing property. Except NH<sub>3</sub>, all the hydrides are strong reducing agents. They react with metal ions (Ag<sup>®</sup>, Cu<sup>2+</sup> to form their phosphides, arsenides and antimonides respectively.

Reducing agent:  $NH_3 > PH_3 > AsH_3 > SbH_3 > BiH_3$ 

4. **Basic character:** Ammonia is the strongest base  $a_{000}$  them. Down the group, the basic character of the hydrides of the elements of group 15 decreases. PH<sub>3</sub> is a  $m_{00}$  weaker base than NH<sub>3</sub>, AsH<sub>3</sub> SbH<sub>3</sub> and BiH<sub>3</sub> are not  $b_{000}$  at all.

**Explanation:** The basic character of the hydrides of  $gr_{0lp}$  15 is due to the lone pair of electrons on the central  $ato_{fl}$  in them (called Lewis bases).

Since the size of nitrogen atom is small, the lone pair of electrons is distributed over a small volume. As a result electron density on N is high and hence ammonia is strongly basic. Down the group, the size of the atoms (P, As, Bi etc.) goes on increasing and the lone pair of electrons is distributed over a large volume. As a result electron density decreases and, therefore, the basic strength of their respective hydrides keeps on decreasing.

5. Solubility: Because of tendency towards hydrogen bonding with water molecules, ammonia is soluble in water while PH<sub>3</sub> and other hydrides are insoluble in water.

Nitrogen and phosphorus form two other important hydrides, i.e. hydrazine  $(N_2H_4)$  and diphosphine  $(P_2H_4)$ 

**Hydrazine:** It is prepared by the oxidation of ammonia with NaOCl (sodium hypochlorite)

$$2NH_3 + NaOC1 \longrightarrow N_2H_4 + NaC1 + H_2O$$
Hydrazine

Hydrazine is a strong reducing agent. Hydrazine and is derivatives are used as rocket fuels.

# 2.5.3 REACTIVITY TOWARDS OXYGEN (OXIDE FORMATION)

Nitrogen due to its small size has a strong tendency to form  $p\pi-p\pi$  multiple bonds between N and O atoms, while other elements of group do not. Hence nitrogen forms a number of oxides which have no P, As, Sb or Bi analogues. For example,  $N_2O$  is known but  $P_2O$  is not known.

### 2.5.4 PROPERTIES OF OXIDES

- 1. Oxides of non-metals are acidic, those of metalloids are amphoteric while those of metals are basic.
- 2. Greater the electronegativity of the element, more acidic is the oxide.
- 3. Among the oxides of the same element, higher the oxidation state of the element, more is its acidic strength.

The oxides of the type E<sub>2</sub>O<sub>3</sub> of N and P are purely acidic that of As, and Sb amphoteric and those of Bi are predominantly basic.

- (1) Acidic strength of oxides of nitrogen increases in the order:  $N_2O < NO < N_2O_3 < N_2O_4 < N_2O_5 < N_2O$  and NO are, however, neutral.
- b. Acidic strength of trioxides follows the order.

$$N_2O_3 > P_4O_6 > As_4O_6 > Sb_4O_6$$

In fact, As<sub>4</sub>O<sub>6</sub> and Sb<sub>4</sub>O<sub>6</sub> are amphoteric while Bi<sub>2</sub>O<sub>3</sub> is basic in nature.

c. Acidic strength of pentoxides follows the order:

$$N_2O_5 > P_4O_{10} > As_4O_{10} > Sb_4O_{10}$$

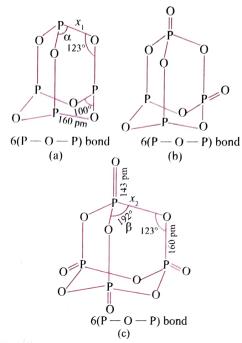
- d. Due to their large size, P, As, Sb and Bi are reluctant to form  $p\pi$ – $p\pi$  multiple bond and their oxides as tetramers,  $X_4O_6$ ,  $X_4O_8$  and  $X_4O_{10}$ . Preparation and properties of oxides of phosphorous are given in the following table and their structures are given below.
- e. Trioxide of As and Sb are prepared by heating the elements in limited supply of oxygen.

$$E_4 + 3O_2 \longrightarrow E_4O_6 (E = As, Sb)$$

Bi<sub>2</sub>O<sub>3</sub> dissolves in acids to give salts

$$Bi_2O_3 + 6HNO_3 \longrightarrow 2Bi(NO_3)_3 + 3H_2O_3$$

Among group 15 elements, Bi alone forms a stable nitrate, sulphate or carbonate and thus behaves like a metal. Structures of P<sub>4</sub>O<sub>6</sub>, P<sub>4</sub>O<sub>8</sub> and P<sub>4</sub>O<sub>6</sub> are given in Fig. 2.2.



**Note**: According to Bent's rule  $x_1 > x_2$  and  $\alpha < \beta$ .

Fig. 2.2 Structure of (a) Phosphorous trioxide (P<sub>4</sub>O<sub>5</sub>), (b)Phosphorous tetroxide  $(P_{\lambda}O_{\lambda})$  and (c) Phosphorous pentoxide  $(P_{\lambda}O_{\lambda})$ 

Table 2.2 Preparation and properties of oxides of phosphorous

Oxides	Oxidation	Preparation	Oxides of arsenic
Phosphorous, P <sub>4</sub> O <sub>6</sub>	+3		<ul> <li>White waxy solid, garlic smell</li> <li>Soluble in ether, benzene, CS<sub>2</sub>, CHCl<sub>3</sub></li> <li>With cold water phosphorous acid is formed P<sub>4</sub>O<sub>6</sub> + 6H<sub>2</sub>O → 4H<sub>3</sub>PO<sub>3</sub></li> <li>With hot water, P<sub>4</sub>O<sub>6</sub> + 6H<sub>2</sub>O → 3H<sub>3</sub>PO<sub>4</sub> + PH<sub>3</sub></li> </ul>
Phosphorous tetraoxides, P <sub>4</sub> O <sub>8</sub>	+4	air	On hydrolysis gives phosphorous acid and phosphoric acid $P_4O_8 + 6H_2O \rightarrow 2H_3PO_3 + 2H_3PO_4$
Phosphorous pentoxide, P <sub>4</sub> O <sub>10</sub>	+5	Heating white $P_4$ in excess of air $P_4 + 5O_2 \rightarrow P_4O_{10}$	<ul> <li>P<sub>4</sub>O<sub>10</sub> + 6H<sub>2</sub>O → 4H<sub>3</sub>PO<sub>4</sub>         Phosphoric acid     </li> <li>Acts as an excellent dehydrating agent 2HClO<sub>4</sub> + P<sub>4</sub>O<sub>10</sub> → Cl<sub>2</sub>O<sub>7</sub> + P<sub>4</sub>O<sub>10</sub> H<sub>2</sub>O</li> </ul>

### 2.5.5 REACTIVITY TOWARDS HALOGENS (HALIDE FORMATION)

Group 15 elements react to form two series of halides:  $EX_3$  and  $EX_5$ .

### 2.5.5.1 Trihalides, $\mathsf{EX}_{\scriptscriptstyle 2}$

1. Preparation: The elements directly combine with halogen to form trihalides, when the group 15 element in excess.

$$\begin{array}{ccc} 2E & + & 3X_2 & \longrightarrow 2EX_3 \\ \text{(Excess)} & \text{Halogen} \end{array}$$

2. Structures: All the trihalides have pyramidal structure. In all the trihalides, the central halogen atom is  $sp^3$  hybridised with 1 lp

Three of the four  $sp^3$  hybrid orbitals overlap with np orbital of the halogen atom to form  $\sigma$  bond. The fourth  $sp^3$  orbital contains lone pair of electrons. According to VSEPR theory, since the lone pair-bond pair (lp-bp) repulsion is greater than bond pair-bond pair (bp-bp) repulsion, contraction in the bond angle occurs, hence bond angle in all the trihalides is less than 109.4° and they have pyramidal shape.

The bond angle of the trihalides of an element increases with the decrease in electronegativity of the halogen atom and increase in the size of the halogen atom.

$$PF_3 < PCl_3 < PBr_3 < PI_3$$

With the decrease in the electron egativity of the halogen atom, bond pairs remain more close to the central atom and hence bp-bp repulsion increases and bond angle increases.

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### 3. Properties:

- a. All the trihalides are predominantly covalent with the ionic character increasing down the group. Thus, BiF3 is predominantly ionic while other halides of Bi, i.e. BiCl<sub>3</sub>, BiBr<sub>3</sub>, etc. and SbF<sub>3</sub> are partly covalent and partly ionic.
- b. Of all the trihalides, trihalides of N, i.e. NCl<sub>3</sub>, NBr<sub>3</sub> and NI, are least stable. However, NF, is stable. NCl<sub>3</sub> is explosive, while NBr<sub>3</sub> and NI<sub>3</sub> are known only as their unstable ammoniates i.e. NBr<sub>3</sub>·NH<sub>3</sub> and NH3·NI3, NI3·NH3 is stable only in moist state. In dry state it explodes with noise when struck liberating vapours of l2. Thus it is a mild and harmless explosive.

$$8 \text{ NI}_3 \cdot \text{NH}_3 \longrightarrow 5 \text{N}_2 + 6 \text{NH}_4 \text{I}$$

The instability of NCl<sub>3</sub>, NBr<sub>3</sub> and NI<sub>4</sub> is due to weakness of N-X bond due to large difference in size of N and X atoms. In NF<sub>3</sub>, as the difference in size of N (75 pm) and F (172 pm) is small N-F bond is quite strong. Consequently, NF3 does not undergo hydrolysis with water, dilute acids or alkalies.

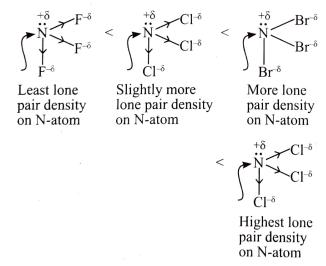
c. Lewis base strength of NX<sub>3</sub>: Due to the presence of lone pair of electrons on N-atom and absence of d-orbitals, N-atom donates its lone pair of electrons and thus behave as Lewis bases. NF, behaves differently from the others. It is unreactive like CF<sub>4</sub> and does not hydrolyse with H,O, dilute acids or alkalis, but reacts if sparkled with water vapour.

$$2NF_3 + 3H_2O \longrightarrow 6HF + N_2O_3$$

Lewis base strength decreases from NF<sub>3</sub> to NI<sub>3</sub>, i.e.

$$NF_3 < NCl_3 < NBr_3 < NI_3$$

With the increase in electronegativity of halogen atom, the bond pair of N-X shifts more and more towards X-atom, hence availability of lone pair on N-atom for donation decreases and Lewis base strength decreases from NF<sub>2</sub> to NI<sub>3</sub> (EN order: F > Cl > Br > I).



#### d. Lewis acid strength of trihalides of P, As and Sb:

The trihalides of P, As, Sb (especially the fluorides and chlorides) due to the presence of d-orbitals, accept lone pair of electrons and thus behaves as Lewis acids, e.g.,

i. 
$$PF_3 + 2F^{\Theta} \longrightarrow [PF_5]^{2-}$$

ii. 
$$SbF_3 + 2F^{\odot} \longrightarrow [SbF_5]^{2-}$$
  
iii.  $2SbF_5 + F^{\odot} \longrightarrow [Sb_2F_7]^{\odot}$   
iv.  $SbCl_3 + 2Cl^{\odot} \longrightarrow [SbCl_5]^{2-}$   
 $F \longrightarrow E$   
 $E \longrightarrow E$ 

Vacant d-orbital

Note: PF3 can act as donor molecules using their lone pair to form a coordinate bond. It is very similar to CO as a ligand. PF<sub>3</sub> is less reactive towards water and is more easily handled than other halides.

- e. Hydrolysis: Trihalides readily undergo hydrolysis but the product of hydrolysis depends on the nature of the bond and on the element.
  - NF, does not undergo hydrolysis, due to high N-F bond strength.
  - ii. Hydrolysis of NCl<sub>3</sub>:

$$NCl_{3} + 3H_{2}O \longrightarrow NH_{3} + 3HOCl$$

$$\downarrow O \\ \downarrow O \\ \downarrow Cl \\ \downarrow Cl \\ \downarrow A \\ \downarrow Cl \\ \downarrow Cl \\ \downarrow A \\ \downarrow Cl \\ \downarrow$$

In NCl<sub>3</sub>, N is more electronegative than Cl, hence N interacts with the positive part of H<sub>2</sub>O molecule and NH, molecule is formed, resulting in the elimination of hypochlorous acid (HOCl)

### iii. Hydrolysis of PCl3:

$$PCl_3 + 3H_2O \longrightarrow H_3PO_3 + 3HCl$$

On the other hand in PCl<sub>3</sub>, P is less electronegative than Cl and P has vacant d-orbital, hence P interacts with negative part of H<sub>2</sub>O molecule resulting in the formation of P—OH bond and elimination of HCl molecule. Consequently H<sub>3</sub>PO<sub>3</sub> is formed on hydrolysis of PCl<sub>3</sub>.

#### iv. Hydrolysis of AsCl,:

$$AsCl_3 + 3H_2O \longrightarrow H_3AsO_3 + 3HCl$$

Trichlorides of As on hydrolysis gives arsenic acid (H<sub>3</sub>AsO<sub>3</sub>) and HCl.

Trichlorides of Bi and Sb are only partly and reversibly hydrolysed to give HCl and oxychloride of the corresponding metal, i.e.

### v. Hydrolysis of SbCl, and SnCl3:

$$SbCl_3 + H_2O \Longrightarrow SbO^{\oplus}Cl^{\Theta} + 2HCl \longrightarrow SbO^{\oplus}$$
Antimony oxychloride  $+ 3Cl^{\Theta}$ 

$$BiCl_3 + H_2O \Longrightarrow BiO^{\oplus}Cl^{\bigcirc} + 2HCl$$
  
Bismuth oxychloride

According to **Le Chatelier principle**, the addition of excess of HCl suppresses the hydrolysis by shifting the equilibrium to the left.

### 2.5.5.2 Pentahalides, EX<sub>E</sub>

1. Nitrogen does not form pentahalides, NX<sub>5</sub> as N due to absence of d-orbitals in its valence shell cannot expand its coordination number beyond 4.

### Phosphorous pentachloride, PCl<sub>5</sub>:

(1) Phosphorous pentachloride is prepared by the reaction of white phosphorous with excess of dry chlorine or by the action of dry chlorine on phosphorous trichloride.

$$\begin{array}{l} P_{_{4(s)}} + \ 10Cl_{_{2(g)}} {\longrightarrow} \ 4PCl_{_{5(s)}} \\ PCl_{_{3(l)}} + \ Cl_{_{2(g)}} {\longrightarrow} \ PCl_{_{5(s)}} \end{array}$$

**b.** It can also be prepared by the action of sulphuryl chloride (SO<sub>2</sub>Cl<sub>2</sub>) on white phosphorous.

$$P_{_{4(s)}} + 10SO_{2}CI_{_{2(l)}} \longrightarrow 4PCI_{_{5(s)}} + 10SO_{_{2(g)}}$$

c. AsCl<sub>5</sub> is highly reactive and unstable and has only a temporary existence. BiF<sub>5</sub> is highly reactive, and explodes with water, forming O<sub>3</sub> and F<sub>2</sub>O. It oxidises UF<sub>4</sub> to UF<sub>6</sub> and BrF<sub>3</sub> to BrF<sub>5</sub>, and fluorinates hydrocarbons. The pentahalides are prepared as follows:

$$3PCl5 + 5AsF3 \longrightarrow 3PF5 + 5AsCl3$$

$$PCl3 + Cl2 (in CCl4) \longrightarrow PCl5$$

$$2As2O3 + 10F2 \longrightarrow 4AsF5 + 3O2$$

$$2Sb2O3 + 10F2 \longrightarrow 4SbF5 + 3O2$$

$$2Bi + 5F2 \longrightarrow 2BiF5$$

2. All the pentahalides behave as **Lewis acids** due to presence of vacant *d*-orbital on the central atom.

$$MX_5 + X^{\bigcirc} \longrightarrow [MX_6]^{\bigcirc}$$

3. PF<sub>5</sub> does not undergo hydrolysis due to high stability of P-F bond as compared to P-O bond. However, all other pentahalides of P, undergo hydrolysis to give POCl<sub>3</sub> initially and with excess of H<sub>2</sub>O gives H<sub>3</sub>PO<sub>4</sub>.

$$PCl_5 + H_2O \longrightarrow POCl_3 + 2HCl$$

$$POCl_3 + 3H_2O \longrightarrow H_3PO_4 + 3HCl$$

$$PCl_5 + 4H_2O \longrightarrow H_3PO_4 + 5HCl$$

4. Pentahalides are thermally less stable than the corresponding trihalides, e.g. thermal stability of PCl<sub>5</sub> is less than PCl<sub>3</sub>.
PCl<sub>5</sub> → PCl<sub>3</sub> + Cl<sub>3</sub>

That is why PCl, behaves as a good chlorinating agent.

5. Structure: In gaseous state, PX<sub>5</sub> are covalent and have trigonal bipyramidal structure as P is sp<sup>3</sup>d hybridised. Whereas in solid state, pentahalides of phosphorous are ionic and exist as given below.

PX <sub>5</sub>	Gas	Solid
Phosphorous pentachloride	PCl <sub>5</sub>	[PCl₄] <sup>⊕</sup> [PCl <sub>6</sub> ] <sup>⊝</sup>
Phosphorous pentabromide	PBr <sub>5</sub>	$[PBr_4]^{\oplus}[Br]^{\Theta}$
Phosphorous pentaiodide	PI <sub>5</sub>	[PI <sub>4</sub> ] <sup>⊕</sup> [I] <sup>⊝</sup>

#### 2.5.6 REACTIVITY TOWARDS METALS

- 1. All the group 15 elements react with metals to form their binary compounds exhibiting -3 oxidation state, such as Ca<sub>3</sub>N<sub>2</sub> (calcium nitride), Ca<sub>3</sub>P<sub>2</sub> (calcium phosphide) Na<sub>3</sub>As<sub>2</sub> (sodium arsenide), Zn<sub>3</sub>Sb<sub>2</sub> (zinc antimonide) and Mg<sub>3</sub>Bi<sub>2</sub> (magnesium bismuthide).
- 2. Sulphide formation: Except nitrogen all other group 15 elements form sulphides. The sulphides of arsenic and antimony are soluble in yellow ammonium sulphide or ammonium sulphide and form thio-compounds.

$$As_2S_3 + 3(NH_4)_2S \longrightarrow 2(NH_4)_3AsS_3$$
  
Ammonium thio-arsenite

$$As_2S_5 + 3(NH_4)_2S \longrightarrow 2(NH_4)_5AsS_4$$
  
Ammonium thio-arsenate

Antimony sulphides form similar compounds. The sulphides are also soluble in alkali.

$$As_2S_3 + 6NaOH \longrightarrow Na_3AsS_3 + Na_3AsO_3 + 3H_2O$$
Sodium thioarsenite

Sodium arsenite

The stability of sulphides increases with increase in atomic number of the element.

# 2.6 ANOMALOUS BEHAVIOUR OF NITROGEN

Nitrogen shows anomalous behaviour and differs from rest of the members of its family due to:

- i. Small size
- ii. High electronegativity
- iii. High ionisation enthalpy
- iv. Non-availability of d-orbitals in its valence shell.

Some important properties in which nitrogen differs from other members of group 15 are as follows:

- 1. Nitrogen exists as a diatomic (N<sub>2</sub>) gas, while others exist as tetrahedra tetraatomic solid molecules (P<sub>4</sub>, As<sub>4</sub> and Sb<sub>4</sub>).
- 2. Nitrogen shows less catenating ability than phosphorous.

- 3. Nitrogen is inert and unreactive in its elemental state, whereas others are highly reactive.
- **4.** Nitrogen due to absence of *d*-orbitals in its valence shell shows a maximum covalency of four, i.e. nitrogen cannot expands its covalency beyond four, e.g. NH<sub>4</sub>. Other group 15 elements due to presence of vacant d-orbitals in their valence shell can have a coordination number 5 or 6 e.g.  $PF_{s}, [PF_{s}]^{\Theta}$ .
- 5. Nitrogen due to absence of d-orbitals in its valence shell, cannot form  $d\pi - p\pi$  bonds, whereas others can. For example, R,N = 0 does not exist, but R,P = 0 exists.
- 6. Due to small size and high electronegativity, nitrogen forms trinegative N<sup>3-</sup> ion. This tendency is less in phosphorous and absent in others.
- 7. Hydride of nitrogen, NH, is stable, while other hydrides are not stable. NH, is capable of forming hydrogen bonding while others do not.
- 8. Nitrogen forms five oxides (N,O, NO, N,O,, NO, or N,O<sub>4</sub> and N<sub>2</sub>O<sub>5</sub>). Whereas, phosphorous forms three dimeric oxides (P<sub>4</sub>O<sub>6</sub>, P<sub>4</sub>O<sub>8</sub>, P<sub>4</sub>O<sub>10</sub>). Arsenic and antimony form only two dimeric oxides (As<sub>4</sub>O<sub>6</sub>, As<sub>4</sub>O<sub>10</sub>, Sb<sub>4</sub>O<sub>6</sub>, Sb<sub>4</sub>O<sub>10</sub>). Bismuth forms Bi,O, only.
- 9. Except NF<sub>3</sub>, the other trihalides of nitrogen, i.e. NCl<sub>3</sub>, NBr<sub>3</sub> and NI, are unstable. On the other hand, trihalides of other elements stable.
- 10. Nitrogen does not form pentahalides, whereas P, As and Sb form pentahalides.
- 11. Nitrogen shows a large number of oxidation states from -3 to +5 other group 15 elements show a limited number of oxidation states.

#### ILLUSTRATION 2.1

- a. Though nitrogen exhibits +5 oxidation state, it does not form pentahalide. Give reason.
- **b.** PH<sub>3</sub> has lower boiling point than NH<sub>3</sub>. Why?
- Sol. **a.** Electronic configuration of nitrogen is  $1s^22s^22p^3$ . Due to absence of d-orbitals in its valence shell. nitrogen cannot expand its coordination number beyond four. That is why nitrogen does not form pentahalides.
  - **b.** Nitrogen is more electronegative than phosphorous and hence capable of forming hydrogen bonds. Due to association of NH, molecules by hydrogen bonding, ammonia has higher boiling point. On the other hand, due to absence of hydrogen bonding in PH<sub>3</sub> molecules are not associated and PH<sub>3</sub> has lower boiling point than NH<sub>3</sub>.

### ILLUSTRATION 2.2

- a. PF, is known, but NF, is not. Why?
- **b.** The experimentally determined N—F bond length in NF. is greater than the sum of single covalent radii of N and F.

- a. Phosphorous has vacant d-orbital in its valence Sol. hence P can have covalency of five and PF s exists But, N due to absence of d-orbital in its valenceshell cannot have covalency of five, hence  $NF_{j_i}$ 
  - b. Due to their smaller size and high electron density experimentally determined N-F bond length is high, because of repulsion of bonded pair of both N and F atoms.

### ILLUSTRATION 2.3

not known.

- a. Why elemental phosphorous does not exist as  $P_2$  like  $N_2$
- b. NCl, gets easily hydrolysed, while NF<sub>3</sub> does not. Why?
- a. Nitrogen due to its small size has a tendency to Sol. form multiple bond and thus exists as diatomic molecule. Phosphorous, on the other hand,  $h_{as}$ comparatively large size, therefore, extent of overlap of (3p-3p) which can result in  $\pi$ -bond formation is less, and phosphorous has no tendency to form multiple bond with itself. Hence phosphorous does not exist as P, molecule.
  - b. In NCl,, N is more electronegative than Cl, hence N has  $\delta$ - charge and Cl has  $\delta$ + charge, moreover due to presence of vacant d-orbital on Cl, it accepts a pair of electron from O atom of H,O molecule. Thus hydrolysis is possible. On the other hand in NF, due to high N-F bond strength, NF, molecule is inert and does not undergo hydrolysis.

#### ILLUSTRATION 2.4

- a. Can PCl, act as an oxidising as well as reducing agent?
- b. Phosphorous does not form phosphorous pentaiodide. Why?
- Sol. a. In PCl<sub>5</sub>, oxidation state of P is +5. Phosphorous can exhibit a maximum oxidation state of +5. Since P cannot have oxidation state greater than +5. Therefore, it cannot get oxidised and thus PCl cannot act as reducing agent. However, P can have lower oxidation state as compared to +5, and thus can get reduced and PCl, behave as oxidising agent
  - b. Due to large size of iodine, phosphorous cannot accommodate five iodine atoms around it, and hence PI<sub>5</sub> does not exist. Moreover EN of iodine is too low to excite  $3s^2$  electron to 3d orbitals for the formation of five bonds.

#### ILLUSTRATION 2.5

- a. Heavier metals of 15 group do not form  $p_{\pi} p_{\pi}$  bonds. Why?
- **b.** Why N—N bond is weaker than single P—P bond.
- **a.** Nitrogen has unique ability to form  $p_{\pi} p_{\pi}$  multiple Sol. bonds with itself and with other elements having small size and high electronegativity (e.g., C, 0) Heavier metals of this group do not form  $p_{\pi} - p_{\pi}$  bonds

as their atomic orbitals are so large and diffuse that they cannot have effective overlapping. Thus, Nitrogen exists as diatomic molecule with a triple bond (one s and two p) between two atoms.

Consequently, its bond enthalpy (971.4 kJ mol<sup>-1</sup>) is very high. On the contrary, P, As and Sb form single bonds as P—P, As—As and Sb—Sb while Bi forms metallic bond in elemental state.

b. It is due to high interelectronic repulsion of the non-bonding e<sup>-s</sup>, owing to the small bond length. As a result catenation tendency is weaker in nitrogen.

## 2.7 DINITROGEN (N<sub>2</sub>)

Nitrogen exists as a diatomic gas,  $N_2$  in the elemental state, hence it is also known as dinitrogen.

### Preparation:

1. Commercial method: Dinitrogen is prepared commercially by the liquefication and fractional distillation of air. On distillation, liquid dinitrogen having lower boiling point (77.2 K) distils out first leaving behind liquid oxygen having higher boiling point (90 K).

#### 2. Laboratory method:

a. By heating an equimolar aqueous solution of ammonium chloride (NH<sub>4</sub>Cl) with sodium nitrite, (NaNO<sub>2</sub>). As a result of double decomposition reaction, ammonium nitrite (NH<sub>4</sub>NO<sub>2</sub>) is formed first, which being unstable decomposes immediately to form dinitrogen gas.

$$\begin{split} & \mathrm{NH_4Cl_{(aq)}} + \mathrm{NaNO_{2(aq)}} \xrightarrow{\quad \mathrm{Heat} \quad} \mathrm{NH_4NO_{2(aq)}} + \mathrm{NaCl_{(aq)}} \\ & \mathrm{NH_4NO_{2(aq)}} \xrightarrow{\quad \mathrm{Heat} \quad} \mathrm{N_{2(g)}} + 2\mathrm{H_2O_{(l)}} \end{split}$$

b. By thermal decomposition of ammonium dichromate:

$$(NH_4)_2Cr_2O_7 \xrightarrow{\text{Heat}} N_2 + 4H_2O + Cr_2O_3$$
Ammonium dichromate oxide (orange) Chromic

c. By thermal decomposition of sodium or barium azide: Very pure nitrogen can be obtained by this method.

$$2\text{NaN}_3 \xrightarrow{\text{Heat}} 2\text{Na} + 3\text{N}_2; \text{ Ba(N}_3)_2 \xrightarrow{\text{Heat}} \text{Ba} + 3\text{N}_2$$

Thermal decomposition of sodium azide is used to inflate the air bags used for safety devices in cars.

# 2.7.1 PROPERTIES

# 2.7.1.1 Physical Properties

1. Dinitrogen is a colourless, odourless, tasteless and non-toxic gas.

2. Nitrogen atom has two stable isotopes: <sup>14</sup>N and <sup>15</sup>N.

3. It has very low solubility in water (23.2 mL/L of water at 273 K and 1 bar pressure).

4. It has low freezing (63.2 K) and boiling point (77.2 K).

5. It is absorbed by activated charcoal.

# 2.7.1.2 Chemical Properties

1. Dinitrogen is an inert gas due to very small N≡N bond length and hence high bond dissociation enthalpy. However, reactivity increases with increase in temperature.

2. **Reaction with metal:** The nitrides formed with active metals are predominantly ionic.

$$6\text{Li} + \text{N}_2 \xrightarrow{\Delta} 2\text{Li}_3\text{N}$$
 (Lithium nitride)  
 $3\text{Mg} + \text{N}_2 \xrightarrow{\Delta} \text{Mg}_3\text{N}_2$  (Magnesium nitride)

- 3. **Reaction with non-metals:** Dinitrogen reacts with non-metals to form predominantly covalent nitrides.
  - **a.** With  $H_2$ ,  $N_2$  reacts at ~773 K and 200 atm in the presence of Fe as catalyst to form ammonia.

$$N_{2(g)} + 3H_{2(g)} = \frac{773 \text{ K}}{200 \text{ atm}} 2NH_{3(g)}$$
 (Haber's process)

**b.** With  $O_2$ ,  $N_2$  combines at a very high temperature, i.e.  $\sim 2000$  K form nitric oxide, NO.  $N_{2(g)} + O_{2(g)} \rightleftharpoons 2NO_{(g)}$ 

#### 4. Reaction with CaC,:

$$\begin{array}{ccc} \operatorname{CaC}_2 + \operatorname{N}_2 & \xrightarrow{\Delta} \operatorname{CaCN}_2 + \operatorname{C} \\ \operatorname{Calcium} & \operatorname{Calcium} \\ \operatorname{carbide} & \operatorname{cyanamide} \end{array}$$

5. Calcium cyanamide reacts with water to form NH<sub>3</sub>, hence, it is used as a fertiliser under the name Nitrolim (CaCN<sub>2</sub> + C).

$$CaCN_2 + 3H_2O \xrightarrow{\Delta} CaCO_3 + 2NH_3$$

#### Uses:

- 1. In the manufacture of ammonia and other industrial chemical containing nitrogen, e.g. calcium cyanamide.
- 2. To provide an inert atmosphere in iron and steel industry. It also acts as a inert diluent (for reactive chemicals).
- 3. Liquid nitrogen is used as a refrigerant, to preserve biological materials, food items and in cryosurgery.
- 4. In gas filled thermometers, which are used for measuring high temperatures.
- 5. To fill electric bulbs, hence reducing the rate of volatilisation of the tungsten filament.

#### 2.7.2 ACTIVE NITROGEN

Active nitrogen is made by passing an electric spark through  $N_2$  gas at 2 mm pressure. This forms atomic nitrogen (N) and the process is associated with yellow-pink after glow. It decomposes many organic compounds.

$$C_2H_2 + 2N \longrightarrow C_2N_2 + H_2$$
  
Cyanogen

# 2.8 AMMONIA (NH<sub>3</sub>)

Ammonia is present in small quantities in air and soil where it is formed by the decay of nitrogenous organic matter, e.g. urea

$$\begin{array}{c} \mathrm{NH_{2}CONH_{2}} + \mathrm{2H_{2}O} \longrightarrow \mathrm{(NH_{4})_{2}CO_{3}} \Longrightarrow \mathrm{2NH_{3}} + \mathrm{H_{2}O} + \mathrm{CO_{2}} \\ \mathrm{Urea} \qquad \qquad \mathrm{Ammonium} \\ \mathrm{carbonate} \end{array}$$

#### Preparation:

(i) 
$$2NH_4Cl + Ca(OH)_2 \xrightarrow{\Delta} 2NH_3 + 2H_2O + CaCl_2$$
  
 $(NH_4)_2SO_4 + 2NaOH \xrightarrow{\Delta} 2NH_3 + 2H_2O + Na_2SO_4$ 

(ii)  $2NH_4Cl + Ca(OH)_2 \xrightarrow{\Delta} 2NH_3 + 2H_2O + CaCl_2$ Slaked lime

#### 2.16 Inorganic Chemistry

- (iii)  $Mg_3N_2 + 6H_2O \longrightarrow 3Mg(OH)_2 + 2NH_3$
- (iv)  $CaO + H_2O \longrightarrow Ca(OH)_2$ 
  - 4. Ammonia cannot be dried by:
    - a. Anhydrous CaCl₂: NH₃ forms a complex with CaCl₂.

      CaCl₂ + 8NH₃ → CaCl₂ · 8NH₃
    - **b. Phosphorous pentoxide:** NH<sub>3</sub> reacts with P<sub>2</sub>O<sub>5</sub> to form ammonium phosphate.

$$P_2O_5 + 3H_2O \longrightarrow 2H_3PO_4$$

$$3NH_3 + H_3PO_4 \longrightarrow (NH_4)_3PO_4$$

c. Concentrated sulphuric acid: NH<sub>3</sub> reacts with conc. H<sub>2</sub>SO<sub>4</sub> to form ammonium sulphate.

$$2NH_3 + H_2SO_4 \longrightarrow (NH_4)_2SO_4$$

Manufacture of ammonia: On commercial scale, ammonia is manufactured by Haber's process.

$$N_{2(g)} + 3H_{2(g)} \Longrightarrow 2NH_{3(g)}$$
  $\Delta_f H^{\odot} = -46.1 \text{ kJ mol}^{-1}$   
This reaction is reversible, exothermic and occurs with decrease in volume. In accordance with **Le Chatelier's principle**, the favourable conditions for the manufacture of ammonia are:

- a. Low temperature: As the forward reaction is exothermic, low temperature will favour the formation of ammonia. The optimum temperature for the reaction has been found to be ~700 K.
- **b. High pressure:** As the forward reaction occurs with decrease in volume, high pressure will favour the formation of ammonia. The optimum pressure for the reaction is about 200 × 10<sup>5</sup> Pa or 200 atm.
- c. Catalyst: Rate of reaction at 700 K and 200 atm pressure is increased by the use of catalyst such as iron oxide with small amount of K<sub>2</sub>O and Al<sub>2</sub>O<sub>3</sub>. Sometimes, molybdenum is used as a promoter (promoter increases the efficiency of the catalyst). Flow chart for the production of ammonia is given in Fig. 2.3.

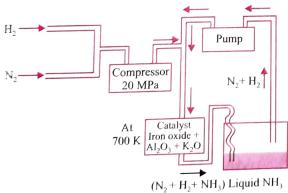


Fig. 2.3 Flow chart for the manufacture of  $\mathrm{NH}_{_3}$  by Haber process

### 2.8.1 PROPERTIES

### 2.8.1.1 Physical Properties

- 1. Ammonia is a colourless gas with a characteristic pungent odour. It brings tears into the eyes.
- **2.** It is lighter than air (density =  $0.68 \text{ g cm}^{-3}$ ).
- 3. It is highly soluble in water. One volume of water dissolves 1300 volumes of ammonia at 0°C at 1 atm pressure. The high solubility in water is due to hydrogen bonding. The

- solubility of ammonia increases with increase of pressure and decreases with increase of temperature.
- 4. It can be easily liquefied at room temperature by the application of pressure. Liquid ammonia is colourless and boils at 239.7 K and freezes at 198.4 K. In the solid and liquid state, it is associated through hydrogen bonds as in the case of water that accounts for its higher boiling and melting points than expected in comparison to other group 15 hydrides, on the basis of its molecular mass.
- 5. On vapourisation, liquid ammonia causes intense cooling.

# 2.8.1.2 Chemical Properties

- Reaction with metals: Ammonia reacts with Na or K metal to form corresponding amides and hydrogen is liberated.
   2Na + NH<sub>3</sub> ---> NaNH<sub>2</sub> + H<sub>2</sub> Sodamide
- 2. Reaction with CO<sub>2</sub>: Liquid NH<sub>3</sub> reacts with gaseous CO<sub>3</sub> at 453–473 K and 220 atmospheres to form ammonium carbonate initially which further decomposes to give urea.

  2NH<sub>3</sub> + CO<sub>2</sub> → NH<sub>2</sub>COONH<sub>4</sub> → NH<sub>2</sub>CONH<sub>2</sub> + H<sub>2</sub>O

  Ammonium Urea Water carbonate

Urea is used as fertiliser as it decomposes slowly in soil to give  $\mathrm{NH_3}$  and  $\mathrm{CO_2}$ .

$$NH_2CONH_2 + H_2O \longrightarrow 2NH_3 + CO_2$$

3. Reaction with Nessler's reagent (test for ammonia):
Ammonia or ammonium salts reacts with Nessler's reagent to give a brown ppt. due to the formation of iodide of Millon's base.

$$2K_2HgI_4 + NH_3 + 3NaOH \longrightarrow H_2N-Hg-O-Hg-I + 7NaI + 2H_0$$

4. Reaction with sodium hypochlorite: When an excess of ammonia solution is boiled with sodium hypochlorite. NaOCl in presence of glue or gelatin, hydrazine is formed.

$$NH_3 + NaOCl \xrightarrow{Fast} NH_2Cl + NaOH$$
 $NH_2Cl + NH_3 \xrightarrow{Slow} NH_2NH_2 + HCl$ 
Chloramine Hydrazine

Glue or gelatin catalyses the slow reaction and prevents the side reaction of the oxidation of hydrazine to nitrogen.

$$N_2H_4 + 2NH_4Cl \longrightarrow N_2 + 2NH_4Cl$$

#### Uses:

- 1. To produce various nitrogeneous fertilisers such is ammonium nitrate, urea, ammonium phosphate, ammonium sulphate, calcium ammonium nitrate (CAN) etc.
- 2. In the manufacture of some inorganic nitrogen compounds such as nitric acid (in Ostwald's process).
- 3. As a cleansing agent for removing grease.
- 4. Liquid ammonia is used as a refrigerant.
- 5. As a laboratory reagent.

# ILLUSTRATION 2.6

- a. Write the reaction of thermal decomposition of sodium azide.
- b. Why does NH<sub>3</sub> act as a Lewis base?

a. Thermal decomposition of sodium azide, NaN, gives N, gas.

$$2\text{NaN}_3 \xrightarrow{\Delta} 2\text{Na} + 3\text{N}_2$$

**b.** Lone pair on N in NH<sub>3</sub> is present in one of the  $sp^3$ hybridised orbital, due to the directional nature of lone-pair of electron on which is available for donation, NH, acts as a Lewis base.

# ILLUSTRATION 2.7

- a. A bottle of liquor ammonia should be cooled before opening. Give reason.
- b. Why conc. H<sub>2</sub>SO<sub>4</sub>, anhydrous CaCl<sub>2</sub> and P<sub>4</sub>O<sub>10</sub> cannot be used as dehydrating agents for ammonia.

Sol.

- a. Liquor ammonia has high vapour pressure at room temperature. Hence, to reduce the vapour pressure inside the bottle in order to avoid bumping, it has to be cooled.
- **b.** Conc.  $H_2SO_4$ , anhydrous  $CaCl_2$  and  $P_4O_{10}$  react with ammonia and hence do not behave as dehydrating agent.

$$H_2SO_4 + 2NH_3 \longrightarrow (NH_4)_2SO_4$$
 $CaCl_2 + 8NH_3 \longrightarrow CaCl_2 \cdot 8NH_3$ 
 $P_4O_{10} + 12NH_3 + 6H_2O \longrightarrow 4(NH_3)_3PO_4$ 

# 2.9 OXIDES OF NITROGEN

Oxides of nitrogen provide a fascinating picture from the point of view of their varied structures and diverse chemical behaviour. They range from  $N_2O$ , NO,  $N_2O_3$ ,  $NO_2$  or  $N_2O_4$  and  $N_2O_5$ . The preparative routes for oxides of nitrogen and their properties are given in following Table 2.3.

Table 2.3 Preparation and properties of oxides of nitrogen.

ble 2.3 Preparation	Formula			Properties
Name	Formula	of nitrogen		1. Colourless, neutral gas
Oinitrogen monoxide OR Nitrous oxide OR	N <sub>2</sub> O	+1	1. $NH_4NO_3 \xrightarrow{250^{\circ}C} N_2O + 2H_2O$ 2. $NH_2OH + HNO_2 \xrightarrow{\Delta} N_2O + 2H_2O$ 3. $Zn + dil \cdot HNO_3 \longrightarrow N_2O + H_2O$	<ol> <li>In solid state, exist as N<sub>2</sub>O·6H<sub>2</sub>O</li> <li>2N<sub>2</sub>O 600°C → 2N<sub>2</sub> + O<sub>2</sub></li> <li>Colourless gas, solid and liquid NO is</li> </ol>
(Laughing gas) Nitrogen monoxide or Nitric oxide	NO	+2	1. $\begin{bmatrix} Cu \longrightarrow Cu^{2+} + 2e^{\Theta} \\ 3e^{\Theta} + NO_3^{\Theta} \longrightarrow NO \end{bmatrix}$ $3Cu + 8HNO_3(dil) \longrightarrow 2NO +$ $3Cu(NO_3)_2 + 4H_2O$	blue in colour. 2. $2NO \xrightarrow{1100^{\circ}C} N_2 + O_2$ 2. $2NO + O \longrightarrow 2NO_2$
			2. Catalytic oxidation of NH <sub>3</sub> $4NH_3 + 5O_2 \xrightarrow{Pt} 4NO + 6H_2O$ 1. NO + NO <sub>3</sub> $\longrightarrow$ N <sub>2</sub> O <sub>3</sub>	1. In solid and liquid state N <sub>2</sub> O <sub>3</sub> is by
Dinitrogen trioxide	N <sub>2</sub> O <sub>3</sub>	+3	1. $NO + NO_2$ $\longrightarrow$ 2. $As_2O_3 + HNO_3(dil) + 2H_2O$ $\longrightarrow$ $N_2O_3 + 2H_3AsO_3$	pletely dissociates to give NO
				Hence in aqueous medium N <sub>2</sub> O <sub>3</sub> acidic in nature.

Nitrogen dioxide	NO,	+4	$\begin{bmatrix} Cu \longrightarrow Cu^{2+} + 2e^{\Theta} \end{bmatrix}$	1. NO <sub>2</sub> is a brown gas, highly
	. 2		$\begin{bmatrix} \operatorname{Cu} \longrightarrow \operatorname{Cu}^{2+} + 2e^{\Theta} \\ \operatorname{NO}_3^{\Theta} + e^{\Theta} + \longrightarrow \operatorname{NO}_2 \end{bmatrix}$	reactive and paramagnetic.
		^	1. Cu + 4HNO <sub>3</sub> (conc.) $\longrightarrow$ 2NO <sub>2</sub> +	
3.0		-		2. Acts as an oxidising agent
			2. $Pb(NO_3)_2 \xrightarrow{\Delta} 2PbO + 4NO_2 + O_2$	$2Cu + NO_2 \longrightarrow CuO + NO$
			(LiNO <sub>3</sub> and Mg(NO <sub>3</sub> ) <sub>2</sub> also give	$2C + 2NO_2 \longrightarrow 2CO_2 + N_2$
			same reaction.	$X_2 + 2NO_2 \longrightarrow 2XNO_2$
				(X = Cl, E
-				3. With strong oxidising agents, higher
			3. NO + $O_2 \longrightarrow NO_2$	oxides of N are formed.
ya x <sup>0</sup>	1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1			$O_3 + 2NO_2 \longrightarrow N_2O_5 + O_2$
Nitrogen tetroxide	N,O <sub>4</sub>	+4	$2NO_2 \xrightarrow{\text{Cooling}} N_2O_4$	1. $N_2O_4 + H_2O \longrightarrow HNO_2 + HNO_3$
indegen renemas	2 4		$2NO_2 = N_2O_4$	2. $N_2O_4 + H_2SO_4(conc.) \longrightarrow$
	:			NO⊕HSO <sub>4</sub> + HN
- + 1 2	, ,			<b>3.</b> Exists in equilibrium with NO both gaseous and liquid state.
Dinitrogenpentoxide	N,O,	+5	1. $2HNO_3 + P_2O_5 \longrightarrow 2HPO_3 + N_2O_5$	1. In solid state, exist as a crystalline
			$2.4 \text{AgNO}_3 + 2 \text{Cl}_2 \longrightarrow 4 \text{AgCl} +$	ionic compound, [NO <sub>3</sub> ] <sup>⊕</sup> (NO <sub>3</sub> ] <sup>⊝</sup> i.e. nitronium nitrate
			$2N_2O_5 + O_2$	In gaseous state, exist as N <sub>2</sub> O <sub>5</sub> having as oxygen bridge, N-O-N
				2. In solid or gaseous state exist as
				$2N_2O_5 \longrightarrow 2N_2O_4 + O_2$
				3. $N_2O_5 + H_2O \longrightarrow 2HNO_3$
				That is why N <sub>2</sub> O <sub>5</sub> is also known as ahydride of HNO <sub>3</sub> . Hence it is acidi in nature.

# 2.9.1 DINITROGEN MONOXIDE OR NITROGEN (I) OXIDE (N,O)

 $N_2O$  acts as better supporter of combustion than air. Reason being, in air % of  $O_2$  is  $\approx$  22%, while  $N_2O$  decomposes to give  $\approx$  33% of  $O_2$ .

$$2N_2O_{(g)} \longrightarrow 2N_{2(g)} + O_{2(g)}$$
  
2 moles 2 moles 1 mole

When inhaled in small amounts, N<sub>2</sub>O induces intoxication and hysterical excitement often accompanied by convulsion laughter hence it is also known as **Laughing gas**. In large amounts, it acts as a narcotic. It is also used as an anaesthetic particularly in dentistry and gynaecology.

### 2.9.2 DINITROGEN OXIDE OR NITRIC OXIDE (NO)

Despite being odd electron the molecule is colourless. This can be explained on the basis of its electronic configuration.

NO (7 + 8 = 15 electrons)  

$$\sigma 1s^2 < \sigma^* 1s^2 < \sigma 2s^2 < \sigma^* 2s^2 < \sigma 2p_z^2 < \pi 2p_y^2 = \pi 2p_x^2 < \pi^* 2p_y^1 < \pi^* 2p_y^0 < \sigma^* 2p_z^0$$

For NO to be coloured, transition from  $\pi^* 2p \longrightarrow \sigma^* 2p$  is required which is forbidden, hence NO is colourless.

B.O. of NO = 
$$1/2$$
 (N<sub>b</sub> - N<sub>a</sub>) =  $1/2$  (10 - 5) = 2.5

NO<sup>⊕</sup> will be more stable than NO molecule, as

B.O. 
$$(NO^{\oplus}) = 1/2 (10 - 4) = 3.0$$

Bond order (B.O.)  $\propto$  Stability

Greater the bond order, greater is the stability of the molecule.

In spite of its reactive and harmful nature, NO occurs in biological system in traces. It acts as a neurotransmitter and plays a significant role in controlling blood pressure by relaxing blood vessels. It also provides protection from bacterial infections.

Nitric oxide and nitrogen dioxide are important in the manufacture of nitric acid and nitrate fertilisers.

### 2.9.3 N<sub>2</sub>O<sub>4</sub>

 $N_2O_4$  is mixed anhydride of HNO<sub>3</sub> and HNO<sub>2</sub> as on reaction with water,  $N_2O_4$  gives HNO<sub>3</sub> and HNO<sub>2</sub>.

$$N_2O_4 + H_2O \longrightarrow HNO_3 + HNO_2$$
Nitric acid Nitrous acid

N<sub>2</sub>O<sub>4</sub> is used as an oxidiser for rocket fuels in missiles and space vehicles.

# 2.9.4 NITRONIUM ION (NO<sub>2</sub><sup> $\oplus$ </sup>)

It is an active electrophilic species present in the mixtures of conc.  $H_2SO_4$  and conc.  $HNO_3$  used as a nitrating mixture in organic chemistry.

 $(HNO_3 conc.) + 2H_2SO_4(conc.) \xrightarrow{\cdot} NO_2^{\oplus} + 2HSO_4^{\ominus} + H_3O^{\oplus}$ 

## 2.9.5 RESONATING STRUCTURE OF NITROGEN OXIDES

1. 
$$N_2O = N_{\frac{113 \text{ pm}}{119 \text{ pm}}} N_{\frac{119 \text{ pm}}{119 \text{ pm}}}O : N = N = N = O.17D$$

2. NO 
$$:N \xrightarrow{\vdots}_{115 \text{ pm}} O: :\dot{N}:=:\ddot{O}:\longleftrightarrow:N:=:\ddot{O}:[OR]:\dot{N}:=:\ddot{O}:\longleftrightarrow:\dot{N}:=:\ddot{O}:$$

[Linear,  $3e^{\Theta}$  bond, paramagnetic in gaseous state. Diamagnetic in solid and liquid state due to dimerisation]

[Odd electron, paramagnetic. Dimerises on cooling to N<sub>2</sub>O<sub>4</sub>.]

4. 
$$N_2O_3$$

$$(Planar)$$

$$(O)$$

(Diamagnetic, dissociate on heating to NO<sub>2</sub>)

[Solid  $N_2O_5$  exists as  $[NO_2]^{\oplus}$   $[NO_3]^{\ominus}$  and is called nitronium nitrate]

Fig. 2.4 Resonating structures of oxides of nitrogen

# 2.10 NITRIC ACID (HNO<sub>3</sub>)

Nitric acid was named aqua fortis (meaning strong water) by Alchemists.

### 2.10.1 PREPARATION

1. In the laboratory: Nitric acid is prepared by heating KNO, or NaNO, and concentrated H2SO4 in glass apparatus since HNO, attacks rubber and cork.

 $NaNO_3 + H_3SO_4 \xrightarrow{Heat} NaHSO_4 + HNO_3$ 

2. On commercial scale: It is manufactured mainly by Ostwalds process. This method is based upon the catalytic oxidation of ammonia by atmospheric oxygen.

$$4NH_{3(g)} + 5O_{2(g)} \xrightarrow{\text{Pt/Rh gauge catalyst}} 3NO_{(g)} + 6H_2O_{(g)}$$

Nitric oxide thus formed readily combines with oxygen to give NO,

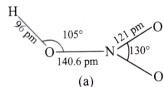
$$2NO_{(g)} + O_{2(g)} \longrightarrow 2NO_{2(g)}$$

Nitrogen dioxide thus formed dissolves in water to form HNO<sub>3</sub>.  $3NO_{2(g)} + H_2O_{(l)} \longrightarrow 2HNO_{3(aq)} + NO_{(g)}$ 

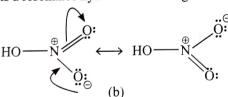
The nitric oxide thus formed is recycled and the aqueous HNO, is concentrated by distillation to give 68% HNO, by mass. (HNO, forms azeotrope at 68% HNO, and 32% water both by mass). Further concentration to 98% can be achieved by dehydration with concentrated H,SO4.

### 2.10.2 STRUCTURE

Spectroscopic studies have shown that in the gaseous state, HNO, exists as a planar molecule.



Nitric acid is a resonance hybrid of following:



### 2.10.5 REACTION OF DIFFERENT ELEMENT WITH HNO,

These are summarised in Table 2.4.

## Table 2.4 Reactions of different elements with HNO

Different concentration of nitric acid	Element	Main products
Conc. HNO <sub>3</sub>	Cu, Ag, Hg, Pb Zn	Metal nitrate + NO <sub>2</sub>
$(NO_3^{\Theta} + 2H^{\oplus} + e^{\Theta} \longrightarrow NO_2 + H_2O)$	Fe, Al, Co, Ni, Cr	Rendered passive
('n' factor = 1)	Sn	Metastannic acid or hydrate oxide (H,SnO <sub>3</sub> ) and NO <sub>3</sub>
Moderately conc. HNO <sub>3</sub>	Fe	Ferric nitrate and NO,
Dilute HNO <sub>3</sub>	Cu, Ag, Hg, Pb	Metal nitrates and NO
$4H^{\oplus} + NO_3^{\ominus} + 3e^{\ominus} \longrightarrow NO + 3H_2O)$ ('n' factor = 3)	<b>a.</b> More active metals with dil. HNO <sub>3</sub> like Zn, Fe, Sn <b>b.</b> $2NO_3^{\ominus} + 10H^{\oplus} + 8e^{\ominus} \longrightarrow N_2O + 5H_2O$ ('n' factor = $8/2 = 4$ )	Metal nitrates and N <sub>2</sub> O

# 2.10.3 PHYSICAL PROPERTIES

- 1. Pure HNO<sub>3</sub> is colourless liquid with pungent odour (freezing point 231.4 K and boiling point 355.6 K). However, impure HNO<sub>3</sub> is yellow due to the presence of dissolved NO<sub>3</sub>.
- 2. Laboratory grade HNO<sub>3</sub> contains ~ 68% of the HNO<sub>3</sub> by mass and has specific gravity of 1.504.
- 3. Fuming nitric acid is pure nitric acid with dissolved NO in it.

# 2.10.4 CHEMICAL PROPERTIES

1. On heating, HNO, decomposes to give nitrogen dioxide oxygen and water.

$$4\text{HNO}_{3(\text{aq})} \xrightarrow{\Delta} 4\text{NO}_{2(\text{g})} + \text{O}_{2(\text{g})} + 2\text{H}_2\text{O}_{(\text{I})}$$

2. Nitric acid is stored in brown coloured gas bottles, in prevent photochemical decomposition of HNO,.

$$2HNO_3 \xrightarrow{hv} 2NO_2 + H_2O + 1/2 O_2$$

3. HNO, behaves as strong monobasic acid and ionises as follows:

$$HNO_3 + H_2O \longrightarrow H_3O^{\oplus} + NO_3^{\bigcirc}$$

In reacts with basic oxides, carbonates, bicarbonates and hydroxides to form corresponding salts.

$$CaO + 2HNO_3 \longrightarrow Ca(NO_3)_2 + H_2O$$

$$Na_2CO_3 + 2HNO_3 \longrightarrow 2NaNO_3 + H_2O + CO_2$$

$$NaOH + HNO_3 \longrightarrow NaNO_3 + H_2O$$

4. Oxidising nature: Nitric acid acts as strong oxidising agent as it decomposes to give nascent oxygen easily.

$$2HNO_3 \longrightarrow H_2O + 2NO_2 + [O]$$

$$2HNO_3 \longrightarrow H_2O + NO + [O]$$

Most of the metals except noble metals like Au and Pt react with HNO3. Some metals like Fe, Al, Co, Ni and Cr do not dissolve in conc. HNO, because of the formation of a layer of oxide on the metal surface, thus these metals are rendered passive.

$\frac{1. \text{ Very diff} = 3}{10 \text{H}^{\oplus} + 8e^{\Theta} + \text{NO}_3} \longrightarrow \text{NH}_4^{\oplus} + 3\text{H}_2\text{O}$		Metal nitrates and hydroxylamine (NH <sub>2</sub> OH) or NH <sub>4</sub> <sup>⊕</sup> ion <b>or</b> ammonium nitrate (NH <sub>4</sub> NO <sub>3</sub> )
2. Cold dil. HNO <sub>3</sub> $7H^{\oplus} + 6e^{\Theta} + NO_3^{\Theta} \longrightarrow NH_2OH + 2H_2O$	Mg, Mn	Metal nitrates and H <sub>2</sub>
(n', factor = 6)		
Aqua regia (conc. HCl: conc. HNO <sub>3</sub> = 3:1)	Noble metals like Au, Pt	Complex ions such as $[AuCl_4]^{\Theta}$ , $[PtCl_6]^{2-}$ and $NO_{(g)}$

2. Conc.  $HNO_3$  ( $NO_3^{\Theta} \longrightarrow NO_3$ ) (n = 1)

Note: 'n' factor for different concentration of HNO,

- 1. As an acid:  $HNO_3 \longrightarrow H^{\oplus}$  (n = 1)
- 3. Dilute HNO<sub>3</sub> (NO<sub>3</sub>  $\hookrightarrow$  NO) (n = 3)
- **4.** Dilute  $HNO_3$  + to give  $N_2O$  with Zn, Fe, Sn.  $(NO_3^{\Theta} \longrightarrow N_2O)$  (n = 4)5. Cold dil. HNO<sub>3</sub> (NO<sub>3</sub>  $\longrightarrow$  NH,OH) (n = 6)
  - **6.** Very dil.  $HNO_{3}$  ( $NO_{3}^{\Theta} \longrightarrow NH_{4}^{\Theta}$ ) (n = 8)layer of oxide is formed on Fe, Al, Co, Ni and Cr with conc. HNO, which prevents the further action of conc. HNO<sub>1</sub>.
    - (C) Sn is oxidised to metastannic acid

$$Sn + 3H_2O \longrightarrow SnO_3^{2-} + 6H^{\oplus} + 4e^{\Theta}$$
$$[NO_3^{\Theta} + 2H^{\oplus} + e^{\Theta} \longrightarrow NO_2 + H_2O] \times 4$$

$$Sn + 4NO_3^{\ominus} + 2H^{\oplus} \longrightarrow SnO_3^{2-} + 4NO_2 + H_2O$$
Add  $2H^{\oplus}$  ion to both sides to get molecular equation

or  $Sn + 4HNO_3^{\ominus} \longrightarrow H_2SnO_3 + 4NO_3 + H_2O_3$ 

(D) With moderately conc. H,SO, Fe gives ferric nitrate, HNO, is reduced to NO<sub>2</sub>.

Fe 
$$\longrightarrow$$
 Fe<sup>3+</sup> + 3e <sup>$\ominus$</sup>   
[NO<sub>3</sub> $^{\ominus}$  + 2H $^{\oplus}$  + e $^{\ominus}$   $\longrightarrow$  NO<sub>2</sub> + H<sub>2</sub>O] × 3  
Fe + 3NO<sub>3</sub> $^{\ominus}$  + 6H $^{\oplus}$   $\longrightarrow$  Fe<sup>3+</sup> + 3NO<sub>2</sub> + 3H<sub>2</sub>O

Add 3NO<sub>3</sub> oion to both sides to get molecular equation or Fe + 6HNO<sub>3</sub> $\longrightarrow$  Fe(NO<sub>3</sub>)<sub>3</sub> + 3NO<sub>2</sub> + 3H<sub>2</sub>O

- (E) With dil HNO,:
  - I. Cu, Ag, Hg, Pb reacts with dil. HNO, to give metal nitrate and HNO, is reduced to NO.

i. 
$$[Cu \longrightarrow Cu^{2+} + 2e^{\Theta}] \times 2$$

$$[NO_3^{\Theta} + 4H^{\oplus} + 3e^{\Theta} \longrightarrow NO + 2H_2O] \times 2$$

$$3Cu + 2NO_3^{\Theta} + 8H^{\oplus} \longrightarrow 3Cu^{2+} + 2NO + 4H_2O$$

Add 6NO, oion to both sides to get molecular equation or  $3Cu + 8HNO_3 \longrightarrow 3Cu(NO_3)_2 + 2NO + 4H_2O$ 

ii. 
$$[Ag \longrightarrow Ag^{\oplus} + e^{\bigodot}] \times 3$$

$$NO_3^{\bigodot} + 4H^{\oplus} + 3e^{\bigodot} \longrightarrow NO + 2H_2O$$

$$3Ag + NO_3^{\bigodot} + 4H^{\oplus} \longrightarrow 3Ag^{\oplus} + NO + 2H_2O$$

Add 3NO<sub>3</sub> oion to both sides to get molecular equation or  $3Ag + 4HNO_3 \longrightarrow 3AgNO_3 + NO + 2H_2O$ 

iii. 
$$[2\text{Hg} \longrightarrow \text{Hg}_2^{2+} + 2e^{\Theta}] \times 3$$
  
 $[\text{NO}_3^{\Theta} + 4\text{H}^{\oplus} + 3e^{\Theta} \longrightarrow \text{NO} + 2\text{H}_2^{\bullet}] \times 2$   
 $6\text{Hg} + 2\text{NO}_3^{\Theta} + 8\text{H}^{\oplus} \longrightarrow 3\text{Hg}_2^{2+} + 2\text{NO} + 2\text{H}_2^{\bullet}$ 

Add.6NO<sub>3</sub> oion to both sides to get molecular equation or  $6Hg + 8HNO_3 \longrightarrow 3Hg_2(NO_3)_2 + 2NO + 2H_2O$ 

### (A) Reactions with conc. HNO,

i. Cu, Ag, Hg, Pb, Zn react with conc. HNO, to form metal nitrates, and NO<sub>3</sub> is reduced to NO<sub>2</sub>.

$$(Cu \longrightarrow Cu^{2+} + 2e^{\Theta}, NO_3^{\Theta} + e^{\Theta} \longrightarrow NO_2)$$

$$Cu \longrightarrow Cu^{2+} + 2e^{\Theta}$$

$$[e^{\Theta} + 2H^{\oplus} + NO_3^{\Theta} \longrightarrow NO_2 + H_2O] \times 2$$

$$\underbrace{[e^{\Theta} + 2H^{\oplus} + NO_3^{\Theta} \longrightarrow NO_2 + H_2O] \times 2}_{\text{Cu} + 4H^{\oplus} + 2NO_3^{\Theta} \longrightarrow \text{Cu}^{2+} + 2NO_2 + 2H_2O}$$

Add 2NO<sub>3</sub> ion to both sides to get molecular equation or  $Cu + 4HNO_3 \longrightarrow Cu(NO_3)_2 + 2NO_2 + 2H_2O$ 

ii. 
$$(Ag \longrightarrow Ag^{\oplus} + e^{\ominus}, NO_3^{\ominus} + e^{\ominus} + NO_2)$$

$$Ag \longrightarrow Ag^{\oplus} + e^{\Theta}$$

$$[NO_3^{\ominus} + 2H^{\oplus} + e^{\ominus} \longrightarrow NO_7 + H_7O_7]$$

$$\frac{[\text{NO}_3^{\ominus} + 2\text{H}^{\oplus} + e^{\ominus} \longrightarrow \text{NO}_2 + \text{H}_2\text{O}}{\text{Ag} + 2\text{H}^{\oplus} + \text{NO}_3^{\ominus} \longrightarrow \text{Ag}^{\oplus} + \text{NO}_2 + \text{H}_2\text{O}}$$

Add 2NO, o ion to both sides to get molecular equation or  $AgNO_3 + 2HNO_3 \longrightarrow AgNO_3 + NO_2 + H_2O_3$ 

iii. (Pb 
$$\longrightarrow$$
 Pb<sup>2+</sup> + 2 $e^{\ominus}$ , NO<sub>3</sub> $\ominus$  +  $e^{\ominus}$  + NO<sub>2</sub>)

$$Pb \longrightarrow Pb^{2+} + 2e^{\Theta}$$

$$[NO_3^{\ominus} + 2H^{\oplus} + e^{\ominus} \longrightarrow NO_2 + H_2O] \times 2$$

$$Pb + 2NO_3^{\ominus} + 4H^{\oplus} \longrightarrow Pb^{2+} + 2NO_2 + 2H_2O$$

Add  $2NO_3^{\Theta}$  ion to both sides to get molecular equation or Pb + 4HNO<sub>3</sub>  $\longrightarrow$  Pb(NO<sub>3</sub>)<sub>2</sub> + 2NO<sub>2</sub> + 2H<sub>2</sub>O

iv.  $(2\text{Hg} \longrightarrow \text{Hg}_2^{2+}, \text{NO}_3^{\Theta} \longrightarrow \text{NO}_2)$ 

$$2 \text{Hg} \longrightarrow \text{Hg}_2^{2+} + 2e^{\Theta}$$

$$[NO_3^{\Theta} + 2H^{\oplus} + e^{\Theta} \longrightarrow NO_2 + H_2O] \times 2$$

$$2Hg + 2NO_3^{\ominus} + 4H^{\oplus} \longrightarrow Hg_2^{2+} + NO_2 + 2H_2O$$

Add 2NO<sub>3</sub> on to both sides to get molecular equation or  $2Hg + 4HNO_3 \longrightarrow Hg_2(NO_3)_2 + 2NO + 2H_2O$ 

v. 
$$(Zn \longrightarrow Zn^{2+}, NO_3^{\Theta} \longrightarrow NO_2)$$

$$Zn \longrightarrow Zn^{2+} + 2e^{\Theta}$$

$$\frac{[\text{NO}_3^{\ominus} + 2\text{H}^{\oplus} + e^{\ominus} \longrightarrow \text{NO}_2 + \text{H}_2\text{O}] \times 2}{\text{Zn} + 2\text{NO}_3^{\ominus} + 4\text{H}^{\oplus} \longrightarrow \text{Zn}^{2+} + 2\text{NO}_2 + 2\text{H}_2\text{O}}$$

Add 2NO<sub>3</sub> on to both sides to get molecular equation or  $Zn + 4HNO_3 \longrightarrow Zn(NO_3)_2 + 2NO_2 + 2H_2O_3$ 

(B) Fe, Al, Co, Ni and Cr are rendered passive with conc. HNO<sub>3</sub>. The inertness exhibited by metals under conditions in which chemical activity is expected is known as passivity. A thin

iv. 
$$[Pb \longrightarrow Pb^{2+} + 2e^{\Theta}] \times 3$$

$$[NO_3^{\Theta} + 4H^{\oplus} + 3e^{\Theta} \longrightarrow NO + 2H_2O] \times 2$$

$$3Pb + 2NO_3^{\Theta} + 8H^{\oplus} \longrightarrow 3Pb^{2+} + 2NO + 2H_2O$$

Add  $6NO_3^{\odot}$ ion to both sides to get molecular equation or  $3Pb + 8HNO_3 \longrightarrow 3Pb_2(NO_3)_2 + 2NO + 4H_2O$ 

II. Zn, Fe, and Sn reacts with dil. HNO<sub>3</sub> to form metal nitrates and HNO<sub>3</sub> is reduced ton N<sub>2</sub>O.

i. 
$$[Zn \longrightarrow Zn^{2+} + 2e^{\Theta}] \times 4$$

$$2NO_3^{\Theta} + 10H^{\oplus} + 8e^{\Theta} \longrightarrow N_2O + 5H_2O$$

$$4Zn + 2NO_3^{\Theta} + 10H^{\oplus} \longrightarrow 4Zn^{2+} + N_2O + 5H_2O$$

Add  $8NO_3^{\Theta}$  ion to both sides to get molecular equation or  $4Zn + 10HNO_3 \longrightarrow 4Zn(NO_3)_2 + N_2O + 5H_2O$ 

ii. 
$$[Fe \longrightarrow Fe^{2+} + 2e^{\Theta}] \times 4$$

$$2NO_3^{\Theta} + 10H^{\oplus} + 8e^{\Theta} \longrightarrow N_2O + 5H_2O$$

$$4Fe + 2NO_3^{\Theta} + 10H^{\oplus} \longrightarrow 4Fe^{2+} + N_2O + 5H_2O$$

Add  $8NO_3^{\odot}$  ion to both sides to get molecular equation or  $4Fe + 10HNO_3 \longrightarrow 4Fe(NO_3)_2 + N_2O + 5H_2O$ 

iii. 
$$[Sn \longrightarrow Sn^{2+} + 2e^{\Theta}] \times 4$$

$$2NO_3^{\Theta} + 10H^{\oplus} + 8e^{\Theta} \longrightarrow N_2O + 5H_2O$$

$$4Sn + 2NO_3^{\Theta} + 10H^{\oplus} \longrightarrow 4Sn^{2+} + N_2O + 5H_2O$$

Add  $8NO_3^{\Theta}$  ion to both sides to get molecular equation or  $4Sn + 10HNO_3 \longrightarrow 4Sn(NO_3)_2 + N_2O + 5H_2O$ 

#### (F) With very dil. HNO3:

- i. Mg and Mn liberate  $H_2$   $Mg + 2HNO_3 \longrightarrow Mg(NO_3)_2 + H_2$  $Mn + 2HNO_3 \longrightarrow Mn(NO_3)_2 + H_2$
- ii. Zn, Fe and Sn form metal nitrates and hydroxylamine or ammonium nitrate

$$4Zn + 10HNO_3 \longrightarrow 4Zn(NO_3)_2 + NH_4NO_3 + 3H_2O$$
  
V. dil

$$4Fe + 10HNO_3 \longrightarrow 4Fe(NO_3)_2 + NH_4NO_3 + 3H_2O$$
$$4Sn + 10HNO_3 \longrightarrow 4Sn(NO_3)_2 + NH_4NO_3 + 3H_2O$$

### Ionic equation:

Fe 
$$\longrightarrow$$
 Fe<sup>2+</sup> + 2e <sup>$\bigcirc$</sup> ] × 4  
 $10H^{\oplus}$  + NO<sub>3</sub> $^{\bigcirc}$  + 8e $^{\bigcirc}$   $\longrightarrow$  NH<sub>4</sub> $^{\oplus}$  + 3H<sub>2</sub>O  
4Fe + NO<sub>3</sub> $^{\bigcirc}$  + 10H $^{\oplus}$   $\longrightarrow$  NH<sub>4</sub> $^{\oplus}$  + 4Fe<sup>2+</sup> + 3H<sub>2</sub>O

Add  $9NO_3^{\Theta}$ ion to both sides to get molecular equation. Similarly, ionic equation for Sn and Zn can be written.

(G) Noble metals like gold, platinum, iridium, rhodium etc. do not react in HNO<sub>3</sub>. However, these metals dissolve in aqua regia (3 parts of conc. HCl and one part of conc. HNO<sub>3</sub>) due to formation of chlorocomplexes such as AuCl<sub>4</sub> O, PtCl<sub>6</sub> 2- etc.

$$HNO_3 + 3HCl \longrightarrow NOCl + Cl_2 + 2H_2O$$
  
 $4Au + 11HCl \longrightarrow 2HAuCl_4 + 6H_2O + 3NOCl$   
Chloroauric acid

### Ionic equations:

$$Au + 4H^{\oplus} + 4Cl^{\Theta} \longrightarrow AuCl_{4}^{\Theta} + NO + 2H_{2}O$$

$$3Pt + 16H^{\oplus} + 4NO_{3}^{\Theta} + 8Cl^{\Theta} \longrightarrow 3PtCl_{6}^{2\Theta} + 4NO + 8H_{5}O$$

- i. Cane sugar is oxidised to oxalic acid on reacting with  $H_{N_0}^{2^3}$  $C_{12}H_{22}O_{11} + 36HNO_3 \longrightarrow 6(COOH)_2 + 36NO_2 + 23H_{20}O_3$
- ii. Nitric acid reacts with proteins forming xanthoprotein, yellow nitro compound. It therefore stains skin and render wool yellow. This property is used for the test of proteins
- iii. Oxidation of non-metals: Dilute HNO<sub>3</sub> does not react with non-metals. But conc. HNO<sub>3</sub> oxidises non-metals such as CS, I and metalloids such as As, Sb, etc. to their corresponding oxyacids, while nitric acid is reduced to NO<sub>2</sub>.

a. 
$$C + 2H_2O \longrightarrow CO_2 + 4H^{\oplus} + 4e^{\Theta}$$

$$[e^{\Theta} + 2H^{\oplus} + NO_3^{\Theta} \longrightarrow NO_2 + H_2O] \times 4$$

$$C + 4NO_3^{\Theta} + 4H^{\oplus} \longrightarrow CO_2 + 4NO_2 + 2H_2O$$
or  $C + 4HNO_3 \longrightarrow CO_2 + 4NO_2 + 2H_2O$ 

b. 
$$[S \longrightarrow SO_4^{2-}, NO_3^{\Theta} \longrightarrow NO_2]$$
  
 $S + 4H_2O \longrightarrow SO_4^{2-} + 8H^{\oplus} + 6e^{\Theta}$   
 $[NO_3^{\Theta} + e^{\Theta} + 2H^{\oplus} \longrightarrow NO_2 + H_2O] \times 6$   
 $S + 6NO_3^{\Theta} + 4H^{\oplus} \longrightarrow SO_4^{2-} + 6NO_2 + 2H_2O$ 

Add  $2H^{\oplus}$  ion to both sides to get molecular equation or  $1/8 S_8 + 6HNO_3 \longrightarrow H_2SO_4 + 6NO_2 + 2H_2O$ 

c. 
$$[I_2 \longrightarrow IO_3^{\ominus}, NO_3^{\ominus} \longrightarrow NO_2]$$
  
 $I_2 + 6H_2O \longrightarrow 2IO_3^{\ominus} + 12H^{\oplus} + 10e^{\ominus}$   
 $[NO_3^{\ominus} + e^{\ominus} + 2H^{\oplus} \longrightarrow NO_2 + H_2O] \times 10$   
 $I_2 + 10NO_3^{\ominus} + 8H^{\oplus} \longrightarrow 2IO_3^{\ominus} + 10NO_2 + 4H_2O$ 

Add  $2H^{\oplus}$  ion to both sides to get molecular equation or  $I_2 + 10HNO_3 \longrightarrow 2HIO_3 + 10NO_2 + 4H_2O$ 

**d.** 
$$[P \longrightarrow PO_4^{3-}, NO_3^{\Theta} \longrightarrow NO_2]$$
  
 $P + 4H_2O \longrightarrow PO_4^{3-} + 8H^{\oplus} + 5e^{\Theta}$   
 $[NO_3^{\Theta} + e^{\Theta} + 2H^{\oplus} \longrightarrow NO_2 + H_2O] \times 5$   
 $P + 5NO_3^{\Theta} + 2H^{\oplus} \longrightarrow PO_4^{3-} + 5NO_2 + H_2O$ 

Add  $3H^{\oplus}$  ion to both sides to get molecular equation or  $1/4 P_4 + 5HNO_3 \longrightarrow H_3PO_4 + 5NO_2 + H_2O$ 

e. 
$$[As \longrightarrow AsO_4^{3-}(Arsenate), NO_3^{\Theta} \longrightarrow NO_2]$$

$$As + 4H_2O \longrightarrow AsO_4^{3-} + 8H^{\oplus} + 5e^{\Theta}$$

$$[NO_3^{\Theta} + e^{\Theta} + 2H^{\oplus} \longrightarrow NO_2 + H_2O] \times 5$$

$$As + 5NO_3^{\Theta} + 2H^{\oplus} \longrightarrow AsO_4^{3-} + 5NO_2 + H_2O$$

Add  $3H^{\oplus}$  ion to both sides to get molecular equation or As + 5HNO<sub>3</sub>  $\longrightarrow$  H<sub>3</sub>AsO<sub>4</sub> + 5NO<sub>2</sub> + H<sub>2</sub>O

f. 
$$[Sb \longrightarrow SbO_4^{3-}(Antimonate), NO_3^{\Theta} \longrightarrow NO_2]$$
  
 $Sb + 4H_2O \longrightarrow SbO_4^{3-} + 8H^{\oplus} + 5e^{\Theta}$   
 $[NO_3^{\Theta} + e^{\Theta} + 2H^{\oplus} \longrightarrow NO_2 + H_2O] \times 5$   
 $Sb + 5NO_3^{\Theta} + 2H^{\oplus} \longrightarrow SbO_4^{3-} + 5NO_2 + H_2O$ 

Add  $3H^{\oplus}$  ion to both sides to get molecular equation or Sb + 5HNO<sub>3</sub>  $\longrightarrow$  H<sub>3</sub>SbO<sub>4</sub> + 5NO<sub>2</sub> + H<sub>2</sub>O

### 2.10.6 USES OF NITRIC ACID

- 1. For purification of Au and Ag.
- 2. In the manufacture of TNT (trinitrotoluene), nitroglycerine and other organic nitro compounds.
- 3. In the pickling of stainless steel.
- 4. In etching of metals and as an oxidiser in rocket fuel.
- **5.** In the manufacture of ammonium nitrate for fertilisers and other nitrates for use in explosives and pyrotechnics.

### 2.10.7 TEST OF NITRATE ION (BROWN RING TEST)

1. [Fe(NO)(H<sub>2</sub>O)<sub>5</sub>]<sup>2+</sup> ion is formed in the brown ring test for the confirmation of nitrate ion in the salt analysis. To the nitrate solution, equal volume of freshly prepared saturated solution of FeSO<sub>4</sub> is added. To this solution, conc. H<sub>2</sub>SO<sub>4</sub> is added slowly from the side of the test tube so that acid forms a layer beneath the mixture. A brown ring is formed at the junction of the two liquids, due to formation [Fe(NO)(H<sub>2</sub>O)<sub>5</sub>](SO<sub>4</sub>).

$$\begin{aligned} &\text{NaNO}_3 + \text{H}_2\text{SO}_4 \longrightarrow \text{NaHSO}_4 + \text{HNO}_2 \uparrow \\ &4\text{FeSO}_4 + 2\text{HNO}_2 + 3\text{H}_2\text{SO}_4 \longrightarrow 3\text{Fe}_2(\text{SO}_4)_3 + 2\text{NO} + 4\text{H}_2\text{O} \\ &\text{FeSO}_4 + \text{NO} + 5\text{H}_2\text{O} \longrightarrow [\text{Fe}(\text{NO})(\text{H}_2\text{O})_5](\text{SO}_4) \\ &\text{Brown ring} \end{aligned}$$

Ionic equations for NO<sub>3</sub><sup>⊙</sup> ion test is represented as:-

$$[Fe^{2+} \longrightarrow Fe^{3+} + e^{\Theta}] \times 3$$

$$4H^{\oplus} + 3e^{\Theta} + NO_{3}^{\Theta} \longrightarrow + NO + 2H_{2}O$$

$$3Fe^{2+} + NO_{3}^{\Theta} + 4H^{\oplus} \longrightarrow 3Fe^{3+} + NO + 2H_{2}O$$

$$FeSO_{4} \cdot 7H_{2}O \text{ is represented as } [Fe(H_{2}O)_{6}]SO_{4} \cdot H_{2}O$$

$$[Fe(H_{2}O)_{6}]^{2+} + NO \longrightarrow [Fe^{+1} (H_{2}O)_{5} NO^{+1}]^{2+} + H_{2}O$$
Brown ring

2. The complex is paramagnetic (n = 3) and  $\mu = \sqrt{15} = 3.83$  BM.

### 2.11 ALLOTROPY

Allotropy is the phenomenon by which an element exists in two or more different crystalline or amorphous forms; and the different forms are called allotropic forms or allotropes of the given element. Different allotropic forms of an element have different physical properties but similar chemical properties.

### 2.11.1 ALLOTROPIC FORMS OF PHOSPHOROUS

Phosphorous is found in various allotropic forms or modifications. Some important allotropes of phosphorous are:

- 1. White or yellow phosphorous
- 2. Red phosphorous
- 3. Black phosphorous

### 2.11.1.1 White Phosphorous

**Preparation:** On heating, phosphate rock, Ca<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub> with coke and sand in an electric furnace at 1773 K, white or yellow phosphorous is obtained.

$$2\text{Ca}_{3}(\text{PO}_{4})_{2} + 6\text{SiO}_{2} \xrightarrow{1773 \text{ K}} 6\text{CaSiO}_{3} + \text{P}_{4}\text{O}_{10}$$

$$P_{4}\text{O}_{10} + 10\text{C} \xrightarrow{1773 \text{ K}} P_{4} + 10\text{CO}$$

**Structure:** White phosphorous exists as tetrahedra tetraatomic discrete  $P_4$  units (Fig. 2.10). The four phosphorous atoms are  $sp^3$  hybridised and lie at the corners of the regular tetrahedron. Each phosphorous atom is linked to each of the other three atoms by covalent bonds. The P-P bond length is equal to 221 pm, and  $\angle PPP = 60^{\circ}$ . Due to high angular strain, white phosphorous is highly reactive.

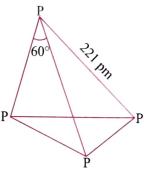


Fig. 2.5 Structure of white P

#### Property:

- 1. On exposure to light, white phosphorous turns yellow, hence it is also known as yellow phosphorous.
- 2. It is soft, translucent waxy solid with garlic odour. Being soft, it can be cut with a knife.
- 3. It is highly poisonous in nature. 0.15 g is the fatal dose. Persons working with phosphorous develop a disease in which the jaw bones decay and the disease is known as **phossy jaw**.
- **4.** The various P<sub>4</sub> molecules are held together by weak van der Waals forces of attraction and hence the melting and boiling points of white phosphorous are quite low.
- **5.** It is insoluble in water but readily dissolves in organic solvents such as CS<sub>2</sub>, alcohol and ether.
- **6.** It contacts with air, it undergoes slow combustion and glows in dark. This property is called **phosphorescence**.
- 7. Its ignition temperature is low (about 30°C). It readily catches fire giving dense fumes of phosphorus pentoxide. It is, therefore, kept under water.

$$P_4 + 5O_2 \longrightarrow P_4O_{10}$$
 or  $2P_2O_5$ 

8. It dissolves in caustic alkalies on boiling in an inert atmosphere and forms phosphine.

$$\begin{array}{c} (0) \\ P_4 + 3 \text{NaOH} + 3 \text{H}_2 \text{O} \longrightarrow 3 \text{NaH}_2 \text{PO}_2 + P \text{H}_3 \uparrow \\ \text{Caustic} \\ \text{soda} \\ \end{array}$$

$$\begin{array}{c} (-3) \\ \text{Sodium hypo-} \\ \text{phosphite} \\ \end{array}$$

It is an example of disproportionation reaction.

9. It directly combines with halogens forming first, trihalides and then pentahalides.

$$P_4 + 6Cl_2 \longrightarrow 4PCl_3$$
;  $P_4 + 10Cl_2 \longrightarrow 4PCl_5$ 

10. It combines with a number of metals forming phosphides.

$$6Mg + P_4 \longrightarrow 2Mg_3P_2$$
 (Magnesium phosphide)  
 $6Ca + P_4 \longrightarrow 2Ca_3P_3$  (Calcium phosphide)

11. It combines with sulphur with explosive violence forming a number of sulphides such as P<sub>2</sub>S<sub>3</sub>, P<sub>2</sub>S<sub>5</sub>, P<sub>4</sub>S<sub>3</sub> and P<sub>4</sub>S<sub>7</sub>.

### 2.11.1.2 Red Phosphorous

**Preparation:** It is obtained by heating white P<sub>4</sub> at 573 K in an inert atmosphere for several days.

$$P_{4(s)} \xrightarrow{573 \text{ K}} P_{4(s)}$$
White phosphorous Red phosphorous

**Structure:** Red phosphorous has polymeric structure, consisting of chains of P<sub>4</sub> tetrahedra linked together through covalent bonds (Fig. 2.6).



Fig. 2.6 Structure of red phosphorous

#### Property:

- 1. It is a hard crystalline odourless solid with iron grey lustre.
- 2. It is non-poisonous in nature.
- 3. It is insoluble in water as well in organic solvents such as CS<sub>2</sub>, alcohol and ether.
- **4.** It is a relatively stable allotrope of phosphorus at room temperature. Its ignition temperature (543 K) is much higher than that of white phosphorus (303 K). Consequently, it does not catch fire easily.
- 5. It sublimes on heating giving vapours which are the same as given by white phosphorus. When these vapours are condensed, white phosphorus is obtained. Thus, red phosphorous is converted into white phosphorous.
- **6.** It is denser (2.16 g cm<sup>-3</sup>) than white phosphorous (1.84 g cm<sup>-3</sup>) and is a bad conductor of electricity.
- 7. Being polymeric in nature, red phosphorous is less reactive than white phosphorus.
- **8.** It burns in oxygen at 565 K to yield phosphorus pentoxide.

$$P_{4(s)} + 5O_{2(g)} \xrightarrow{-565 \text{ K}} P_4O_{10(s)}$$

**9.** Being less reactive than white phosphorus, it reacts with halogens, sulphur and alkali metals only when heated forming their corresponding salts.

$$P_{4} + 6Cl_{2} \xrightarrow{\Delta} 4PCl_{3}; \quad P + 10Cl_{2} \xrightarrow{\Delta} 4PCl_{5}$$

$$8P_{4} + 3S_{8} \xrightarrow{453 \text{ K}} 8P_{4}S_{3}; \quad P_{4} + 12Na \xrightarrow{\Delta} 4Na_{3}P$$

**10.** It does not react with caustic alkalies. This property is made use in separating, red phosphorus from white phosphorus.

### 2.11.1.3 Black Phosphorous

It has two forms: α-black phosphorus and β-black phosphorus.

**1. Preparation:** α-black phosphorus is formed when red phosphorus is heated in a sealed tube at 803 K.

Red phosphorus  $\xrightarrow{453 \text{ K}} \alpha$ -Black phosphorus

 $\beta$ -B1ack phosphorus (orthorhombic) is prepared by heating white phosphorus at 473 K under a very high pressure (4000–12000 atm.) in an inert atmosphere.

White phosphorus  $\xrightarrow{473 \text{ K}} \beta$ -Black phosphorus atm pressure

2. Structure: β-black phosphorus has a layered structure in which each phosphorus atom is covalently bonded to three neighbouring phosphorus atoms as shown in Fig. 2.7. The P—P—P angles are of 99° and P—P distance is 218 pm.

The adjacent layers are held 368 pm apart. The atoms within a layer are more strongly bound than the atoms in adjacent layers. This gives  $\beta$ -black phosphorus graphite like structure

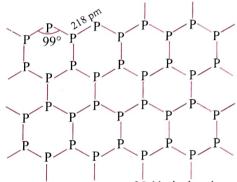


Fig. 2.7 Layered structure of  $\beta$ -black phosphorous

### 3. Properties:

- a. It can be sublimed in air and has opaque monoclinic or rhombohedral crystals.
- **b.** It is a very stable allotrope of phosphorous and does not oxidise in air until heated very strongly.
- c. It is good conductor of electricity.

#### 4. Uses:

- **a.** In the manufacture of food grade phosphates, detergent phosphates and pharmaceuticals.
- **b.** Elemental phosphorous is used in water industry.
- c. In the manufacture of organophosphorous compounds used as pesticides.
- d. In the form of phosphatic fertilisers in agriculture.

# 2.12 PHOSPHINE (PH<sub>3</sub>)

#### **Preparation:**

1. By hydrolysis of metal phosphides such as Ca<sub>3</sub>P<sub>2</sub> or Na<sub>3</sub>P with water or dilute HCl.

$$Ca_3P_2 + 6H_2O \longrightarrow 3Ca(OH)_2 + 2PH_3$$
  
 $Ca_3P_2 + 6HCl \longrightarrow 3CaCl_2 + 2PH_3$ 

2. In laboratory, it is prepared by heating white phosphorous with concentrated NaOH solution in an inert atmosphere of CO<sub>2</sub>. It is disproportionation reaction.

$$P_4 + 3NaOH + 3H_2O \longrightarrow PH_3 + 3NaH_2PO_2$$

Phosphine (Sodium hypophosphite

$$\begin{array}{c} & \Delta \rightarrow \text{Na}_3\text{PO}_4 + \text{PH}_3 \\ & \text{Sodium phosphate} \end{array}$$

$$Zn_3M_2(S) + 6HCl(aq) \longrightarrow 2NH_3(g) + 3ZnCl_2(aq)$$
  
where M = As, Sb.

**Ionic equation:** It is disproportionation reaction in basic medium of  $P_4$  to  $H_2PO_2^{\bigcirc}$  (oxidation) and  $P_4$  to  $PH_3$  (reduction)

$$2 \overset{\bullet}{O} H + 2 \overset{\bullet}{H_2} O + P \longrightarrow \overset{\bullet}{H_2} PO_2 \overset{\ominus}{\circ} + e^{\Theta} + 2 \overset{\bullet}{H_2} O] \times 3$$

$$2 \overset{\bullet}{H_2} O + 3 e^{\Theta} + P \longrightarrow PH_3 + 3 \overset{\bullet}{O} H$$

$$3 \overset{\bullet}{O} H + 3 \overset{\bullet}{H_2} O + 4 P \longrightarrow \overset{\bullet}{H_2} PO_2 \overset{\ominus}{\circ} + PH_3$$

$$\begin{array}{c}
3OH + 3H_2O + 4P \longrightarrow H_2PO_2 + PH_3 \\
\hline
\text{or } 3OH + 3H_2O + P_4 \longrightarrow 3H_2PO_2^{\Theta} + PH_3
\end{array}$$

When pure, PH<sub>3</sub> is non-inflammable but becomes inflammable owing to the presence of P<sub>2</sub>H<sub>6</sub> or P<sub>4</sub> vapours. This is the origin of flickering light called **will-o-the-wisp** which is sometimes seen in marshes. Therefore, a current of CO<sub>2</sub> is passed through the flask to displace air.

To purify it from the impurities, it is absorbed in HI to form phosphonium iodide (PH<sub>4</sub>I) which on treating with KOH gives off phosphine.

$$PH_{J}I + KOH \longrightarrow KI + H_{2}O + PH_{3}$$

3. By heating phosphorous acid:

$$4H_3PO_3 \xrightarrow{\text{Heat}} 3H_3PO_4 + PH_3$$
Phosphorous Phosphoric Phosphine acid acid

Note: 
$$\ddot{P}H_3 + H^{\oplus} \longrightarrow \overset{\oplus}{P}H_4$$

According to Drago's rule lp  $e^-$ 's on P lie in almost pure s-orbital, hence due to non-directional nature, its overlapping tendency is less in comparision to a lp  $e^-$ 's present in hybrid orbitals, which is direction as present  $NH_3$ .

#### **Properties:**

- 1. It is a colourless gas with rotten fish smell and is highly poisonous.
- 2. It is slightly soluble in water, the aqueous solution is neutral.
- 3. Phosphine decomposes on heating in absence of air into its constituent elements, i.e. P<sub>4</sub> and H<sub>2</sub>.

$$4PH_3 \xrightarrow{\Delta} P_4 + 6H_2$$

Solution of  $PH_3$  in water decomposes in presence of light giving red phosphorous and  $H_2$ .

$$4PH_{3(aq)} \xrightarrow{hv} P_{4(s)} + 6H_{2(g)}$$
Red

4. Phosphine explodes in contact with traces of oxidising agent like Cl<sub>2</sub> or Br<sub>2</sub> vapours, HNO<sub>3</sub> etc.

$$PH_3 + 3Cl_2 \longrightarrow PCl_3 + 3HCl$$
  
 $PH_3 + 4Cl_3 \longrightarrow PCl_5 + 3HCl$   
(Excess)

5. Phosphine is feebly basic and like NH<sub>3</sub> forms salts with mineral acids under anhydrous conditions.

$$PH_{3} + HX \longrightarrow PH_{4}^{\oplus}X^{\bigcirc}$$
Phosphine Phosphonium halide (X = Cl, Br, I)

6. When PH<sub>3</sub> is bubbled through the aqueous solutions of copper, and mercury salts, the precipitates of corresponding phosphides are formed.

$$3HgCl_2 + 2PH_3 \longrightarrow Hg_3P_2 \downarrow + 6HCl$$
  
Mercuric chloride Mercuric phosphide

7. With silver nitrate, first a complex of silver phosphide is produced, which is subsequently reduced in presence of water to metallic silver which appears as a black ppt.

$$PH_3 + 6AgNO_3 \longrightarrow Ag_3P \cdot 3AgNO_3 + 3HNO_3$$
Intermediate complex

$$Ag_3P \cdot 3AgNO_3 + 3H_2O \longrightarrow 6Ag \downarrow + 3HNO_3 + H_3PO_3$$
Black ppt.

#### Uses:

- 1. Spontaneous combustion of PH<sub>3</sub>. It is used as Holme's signals in deep seas and oceans for signalling danger points to steamers. Containers containing a mixture of calcium phosphide and calcium carbide are pierced and thrown into the sea. In contact with water, a mixture of phosphine and acetylene gases is produced. Phosphine frequently contains traces of highly inflammable disphosphine P<sub>2</sub>H<sub>4</sub> which catches fire spontaneously. This ignites acetylene which bums with a luminous flame and thus serves as a signal to the approaching ship. That is, PH<sub>3</sub> sometimes called cold fire.
- Shells containing calcium phosphide are exploded by warships. Calcium phosphide reacts with water producing phosphine which burns in air to give clouds of P<sub>4</sub>O<sub>10</sub> which act as smoke screens.

### ILLUSTRATION 2.8

- a. Why does NO, dimerise?
- **b.** In what way can it be proved that PH<sub>3</sub> is basic in nature?

a. NO<sub>2</sub> contains odd number of valence electrons.

It behaves as an odd electron molecule hence it dimerises. On dimerisation, it is converted to stable N<sub>2</sub>O<sub>4</sub> molecule with even number of electrons.

**b.** PH<sub>3</sub> reacts with acids like HI to form PH<sub>4</sub>I which shows that it is basic in nature.

$$PH_3 + HI \longrightarrow PH_4I$$

Due to lone pair of electrons on P in PH<sub>3</sub>, it acts as a Lewis base in the above reaction.

### ILLUSTRATION 2.9

- a, A tetraatomic molecule (A) on reaction with nitrogen (I) oxide, produces two substances (B) and (C). (B) is a dehydrating agent while substance (C) is a diatomic gas which shows almost inert behaviour. Identify (A), (B) and (C).
- **b.** Why red phosphorous is denser and chemically less reactive than white phosphorous?
- c. Why nitrous oxide supports combustion better than air?

Sol.

a. 
$$(A) + N_2O \longrightarrow (B) + (C)$$
Tetraatomic molecule agent gas
$$P_4 + 10N_2O \longrightarrow P_4O_{10} + 10N_2$$
(A) (B) (C)

(A) is tetratomic molecule, which on reaction with nitrogen (I) oxide,  $N_2O$  gives (B), i.e.  $P_4O_{10}$  which acts as a dehydrating agent, while (C) is  $N_2$ , a diatomic gas which is inert.

- **b.** Red phosphorous is regarded as a polymer consisting of chains of P<sub>4</sub> tetrahedra linked together. Hence red phosphorous is denser and less reactive than white phosphorous.
- c. Air has  $\sim 22\%$  O<sub>2</sub> in it, while N<sub>2</sub>O on decomposition produces  $\sim 33\%$  of O<sub>2</sub> by volume.

$$2N_2O \longrightarrow 2N_2 + O_2$$
  
2 vol. 2 vol. 1 vol.

$$O_2 = \frac{\text{Total vol of N}_2 \text{ and } O_2}{3} \approx 33\%$$

Since % of O<sub>2</sub> produced by decomposition of N<sub>2</sub>O is more, it acts as a better supporter of combustion.

### ILLUSTRATION 2.10

- a. What is the role of phosphorous pentoxide in the preparation of N<sub>2</sub>O<sub>5</sub>?
- **b.** Phosphine is prepared in an inert atmosphere of CO<sub>2</sub>. Why?
- c. Red phosphorous is used for making matches. Why?

### Sol

- a. P<sub>4</sub>O<sub>10</sub> acts as strong dehydrating agent. It removes water molecules from nitric acid, HNO<sub>3</sub> to form N<sub>2</sub>O<sub>5</sub>.
   P<sub>4</sub>O<sub>10</sub> + 12HNO<sub>3</sub> → 4H<sub>3</sub>PO<sub>4</sub> + 6N<sub>2</sub>O<sub>5</sub>
- **b.** Phosphine, being inflammable, burns in air. It is therefore prepared in an inert atmosphere.
- **c.** Red phosphorous is non-poisonous and has a high ignition point and hence red phosphorous is used for making matches.

### ILLUSTRATION 2.11

- a. Nitric oxide turns brown in air. Why?
- b. Copper dissolves in HNO<sub>3</sub> but not in HCl. Why?

#### Sol.

a. Nitric oxide directly reacts with oxygen of air and forms nitrogen dioxide, NO<sub>2</sub> which is brown in colour.

$$2NO + O_2 \longrightarrow 2NO_2$$

Colourless (air) Brown coloured gas

**b.** HNO<sub>3</sub> behaves as an oxidising agent and oxidises Cu to Cu<sup>2+</sup>, which dissolves in HNO<sub>3</sub> as copper nitrate. On the other hand, HCl does not behave as an oxidising agent and hence copper does not dissolve in HCl.

### ILLUSTRATION 2.12

Calculate the number of moles of Cu and  $HNO_3$ , when copper reacts with  $HNO_3$  to give NO and  $NO_2$  in the (2:1) molar ratio.

#### Sol.

$$[Cu \longrightarrow Cu^{2+} + 2e^{\Theta}] \times 3$$

$$[NO_3^{\Theta} + 4H^{\oplus} + 4e^{\Theta} \longrightarrow NO + 2H_2O] \times 2$$

$$3Cu + 2NO_3^{\Theta} + 8H^{\oplus} \longrightarrow 3Cu^{2+} + 2NO + 4H_2O$$

Add 6NO<sub>3</sub> to both sides to get the molecular equation.

(or) 
$$3Cu + 8NO_3^{\ominus} + 8H^{\oplus} \longrightarrow 3Cu^{2+} + 6NO_3^{\ominus} + 2NO + 4H_{2O}$$
  
 $3Cu + 8HNO_3 \longrightarrow 3Cu(NO_3)_2 + 2NO + 4H_{2O} \longrightarrow (i)$   
 $3Cu \longrightarrow Cu^{2+} + 2e^{\ominus}$ 

$$Cu \longrightarrow Cu^{2+} + 2e^{\Theta}$$

$$[NO_3^{\Theta} + 2H^{\oplus} + e^{\Theta} \longrightarrow NO_2 + H_2O] \times 2$$

$$Cu + 2NO_3^{\Theta} + 4H^{\oplus} \longrightarrow Cu^{2+} + 2NO_2 + 2H_2O$$

Add 
$$2NO_3^{\ominus}$$
 to both sides to get the molecular equation.  
 $Cu + 4NO_3^{\ominus} + 4H^{\oplus} \longrightarrow Cu^{2+} + 2NO_3^{\ominus} + 2NO_2 + 2H_{2O}$   
or  $Cu + 4HNO_3 \longrightarrow Cu(NO_3)_2 + 2NO_2 + 2H_{2O} \longrightarrow ... (ii)$ 

To get NO and NO<sub>2</sub> in the molar ratio (2 : 1), multiply equation (i) by 2 and then add equation (ii) to it, i.e.  $3\text{Cu} + 8\text{HNO}_3 \longrightarrow 3\text{Cu}(\text{NO}_3)_2 + 2\text{NO} + 2\text{H}_2\text{O}] \times 2$ 

$$Cu + 4HNO_3 \longrightarrow Cu(NO_3)_2 + 2NO_2 + 2H_2O_3$$

$$7\text{Cu} + 20\text{HNO}_3 \longrightarrow 7\text{Cu}(\text{NO}_3)_2 + 6\text{NO}_2 + 10\text{H}_2\text{O}$$

Ans: Moles of Cu = 7, moles of  $HNO_3 = 20$ 

### 2.13 PHOSPHOROUS HALIDES

Phosphorous forms two types of halides:

- 1. Trihalides,  $PX_3$ ; where X = F, Cl, Br and I.
- 2. Pentahides,  $PX_s$ ; where X = F, Cl, Br.

### 2.13.1 PHOSPHOROUS TRICHLORIDE (PCL<sub>3</sub>)

### Preparation:

- 1. By passing dry  $Cl_2$  over heated white phosphorous  $P_4 + 6Cl_2 \longrightarrow 4Cl_3$
- 2. By the action of thionyl chloride on white phosphorous  $P_4 + 8SOC1$ ,  $\longrightarrow 4PC1$ , + 4SO, + 2S, C1,

### 3. Properties:

- a. It is a colourless, pungent smelling oily liquid, which boils at 347 K and solidifies at 161 K.
- **b.** It fumes in moist air as PCl<sub>3</sub> hydrolysis in moist air resulting in the formation of HCl.

$$PCl_3 + 3H_2O \longrightarrow H_3PO_4 + 3HCl$$

4. Reaction with conc.  $H_2SO_4$  $H_2SO_4 + PCl_3 \longrightarrow SO_2Cl_2 + SO_3 + HPO_3 + 2HCl_3$ 

Sulphuric Sulphuryl acid chloride

- PCl<sub>3</sub> acts as reducing agent PCl<sub>3</sub> + SO<sub>3</sub> → POCl<sub>3</sub> + SO<sub>3</sub>
- **6.** It reacts with organic compounds containing OH group where –OH group is replaced by –Cl group, e.g.

$$3CH_3COOH + PCl_3 \longrightarrow 3CH_3COCl + H_3PO_3$$

$$3C_2H_5OH + PCl_3 \longrightarrow 3C_2H_5Cl + H_3PO_3$$

That is why PCl<sub>3</sub> is widely used in organic chemistry <sup>10</sup> convert carboxylic acids to acid chlorides and alcohols <sup>10</sup> alkyl halides.

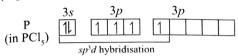
# 2.13.2 PHOSPHOROUS PENTACHLORIDE (PCL<sub>5</sub>)

### Preparation:

By the reaction of white phosphorous with excess of dry Cl₂
 P₄ + 10Cl₂ → 4PCl₅

$$\frac{\text{phosphorous}}{\text{p}_4 + 10\text{SO}_2\text{Cl}_2} \longrightarrow 4\text{PCl}_5 + 10\text{SO}_2$$

3. Structure: P in PCl<sub>5</sub> undergoes  $sp^3d$  hybridisation and PCl<sub>5</sub> has trigonal bipyramidal geometry in gaseous and liquid state (Fig. 2.8).



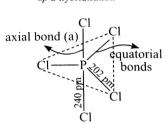
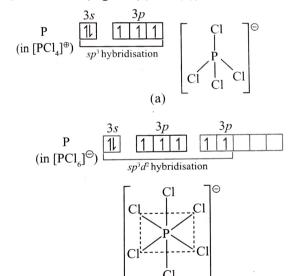


Fig. 2.8 Structure of PCl.

The three equatorial P—Cl bonds are equivalent, while the two axial P—Cl bonds are equivalent and larger than equatorial bonds. ∠ClPCl in equatorial plane is 120°, and in axial plane is 90°.

In the solid state, PCl<sub>5</sub> exists as an ionic solid

 $[PCl_4]^{\oplus}$   $[PCl_6]^{\bigodot}$  in which  $[PCl_4]^{\oplus}$  is tetrahedral while  $[PCl_6]$  is octahedral. (Fig. 2.9(a) and (b))



 ${\rm (b)}$  Fig. 2.9 (a) Structure of  ${\rm [PCl_4]}^{\bigcirc}$  and (b) Structure of  ${\rm [PCl_6]}^{\bigcirc}$ 

### 4. Properties:

- **a.** PCl<sub>5</sub> is a yellowish white crystalline solid with a characteristic smell.
- **b.** In moist air, it hydrolyses to POCl<sub>3</sub> and finally gets converted to phosphoric acid.

$$PCl_5 + H_2O \longrightarrow POCl_3 + 2HCl$$
  
 $POCl_3 + 3H_2O \longrightarrow H_3PO_4 + 3HCl$ 

With excess of water, PCl<sub>5</sub> reacts violently to produce H<sub>3</sub>PO<sub>4</sub> and HCl.

$$PCl_5 + 4H_2O \longrightarrow H_3PO_4 + 5HCl$$
(Excess)

**c.** On heating, it sublimes but decomposes on stronger heating to PCl<sub>3</sub> and Cl<sub>2</sub>.

$$PCl_5 \xrightarrow{Heat} PCl_3 + Cl_2$$

d. PCl<sub>5</sub> converts carboxylic acids to acid chlorides and alcohols to alkyl halides, i.e. it is used in organic synthesis.

$$PCl_5 + 4CH_3COOH \longrightarrow 4CH_3COCl + H_3PO_4 + HCl$$
  
 $PCl_5 + 4C_2H_5OH \longrightarrow 4C_2H_5Cl + H_3PO_4 + HCl$ 

e. PCl<sub>5</sub> reacts with finally divided metal on heating to give corresponding chlorides.

$$2Ag + PCl_5 \longrightarrow AgCl + PCl_3$$
  
 $Sn + 2PCl_5 \longrightarrow SnCl_4 + 2PCl_3$ 

**f.** Reaction with  $P_4O_{10}$ .  $P_4O_{10} + 6PCl_5 \longrightarrow 10POCl_3$ 

g. Reaction with 
$$SO_2$$
.  
 $SO_2 + PCl_5 \longrightarrow POCl_3 + SOCl_2$ 
Thionyl chlorid

### 2.14 OXOACIDS OF PHOSPHOROUS

1. The oxoacids of nitrogen have no phosphorous analogues and although HPO<sub>3</sub> has the same empirical formula as HNO<sub>3</sub>, it is a polymeric compound unlike HNO<sub>3</sub>. The difference lies in the fact that strong  $p\pi$ – $p\pi$  bonding does not occur between phosphorous and oxygen. However, in all the oxyacids of phosphorous and their salts, the terminal P—O bonds are shorter than expected value for a P—O single bond, from which it is assumed that  $\sigma$  bonding between P and O is augmented by  $(p\pi$ – $d\pi)$  bonding between empty 3d orbitals on P and filled 2p orbital on oxygen to give P—O linkages multiple bond character.

The phosphorous oxoacids can be divided into two classes:

- **a.** Phosphorous acids, in which the formal oxidation state of P is +1 and +3.
- **b.** Phosphoric acids, in which the formal oxidation state of P is +5.
- 2. Few important points about oxoacids of phosphorous are as follows:
  - **a.** In all oxoacids, phosphorous is tetrahedrally surrounded by four other atoms or groups.
  - **b.** All these acids contain at least one P = O and one P—OH bond.
  - c. The oxoacids in which phosphorus has oxidation state less than +5, contain, in addition to P = O and P—OH bonds, either P—H (e.g., H<sub>3</sub>PO<sub>2</sub>, H<sub>3</sub>PO<sub>3</sub>) or P—P (e.g., H<sub>4</sub>P<sub>2</sub>O<sub>6</sub>) bonds but not both.
  - **d.** The oxoacids in +3 oxidation state undergo disproportionation reaction to give compounds in lower and higher oxidation states. For example

$$(+3) \qquad (-3) \qquad (+5)$$

$$4H_3PO_3 \xrightarrow{\text{Heat}} PH_3 + 3H_3PO_4$$
Orthophosphorous Phosphine Orthophosphoric acid

- e. Acids which contain P—H bonds have behave as reducing agents. For example, hypophosphorous acid (H<sub>3</sub>PO<sub>2</sub>) is a good reducing agent as it contains two P—H bonds and thus reduces AgNO<sub>3</sub> to metallic silver and HgCl<sub>2</sub> to Hg.
  - $4AgNO_3 + H_3PO_2 + 2H_2O \longrightarrow 4Ag\downarrow + H_3PO_4 + 4HNO_3$   $2HgCl_2 + H_3PO_2 + 2H_2O \longrightarrow 2Hg\downarrow + H_3PO_4 + 4HCl$  $H_3PO_3$  also acts as a reducing agent though weaker than  $H_3PO_2$  because it contains only one P—H bond as compared to two in  $H_3PO_2$ . It reduces acidified KMnO<sub>4</sub>,  $I_2$ , and salts of copper, silver, mercury, etc.
  - i.  $2KMnO_4 + 3H_2SO_4 + 5H_3PO_3 \longrightarrow K_2SO_4 + 2MnSO_4 + 5H_3PO_4 + 3H_2O$
  - ii.  $l_3 + H_3PO_3 + H_2O \longrightarrow H_3PO_4 + 2HI$
  - iii.  $CuSO_4 + H_3PO_3 + H_2O \longrightarrow Cu \downarrow + H_3PO_4 + H_2SO_4$
  - iv.  $2AgNO_3 + H_3PO_3 + H_2O \longrightarrow 2Ag\downarrow + H_3PO_4 +$

2HNO,

v. 
$$2\text{HgCl}_2 + \text{H}_3\text{PO}_3 + \text{H}_2\text{O} \longrightarrow \text{Hg}_2\text{Cl}_2 \downarrow + \text{H}_3\text{PO}_3 + \text{H}_2\text{O} \longrightarrow \text{Hg}_2\text{Cl}_2 \downarrow + \text{H}_3\text{PO}_3 + \text{H}_3\text{PO}_$$

i.  $[MnO_4^{\Theta} \longrightarrow Mn^{2+}; PO_3^{2-} \longrightarrow PO_4^{3-}]$   $8H^{\oplus} + 5e^{\Theta} + MnO_4^{\Theta} \longrightarrow Mn^{2+} + 4H_2O$  $H_2O + PO_3^{2-} \longrightarrow PO_4^{3-} 2H^{\oplus} + e^{\Theta}] \times 5$ 

$$MnO_4^{\Theta} + 5PO_3^{2-} + H_2O \longrightarrow Mn^{2+} + 5PO_4^{3-} + 2H^{9}$$

ii. 
$$2e^{\Theta} + I_2 \longrightarrow 2I^{\Theta}$$
  
 $H_2O + PO_3^{2-} \longrightarrow PO_4^{3-} 2H^{\oplus} + e^{\Theta}] \times 2$   
 $I_2 + 2PO_3^{2-} + 2H_2O \longrightarrow 2PO_4^{3-} + 2I^{\Theta}$ 

Similarly, the ionic equation for reaction (iii), (iv) and (v) can be written.

f. Oxoacids of phosphorous are summarised in Table 2.5

# Table 2.5 Some oxoacids of phosphorous

	Name	Formula and O.S.	Characteristics bonds and their number	Basicity	Methods of preparation
	1. Orthophosphoric acid	H <sub>3</sub> PO <sub>4</sub> (+5)	Three P—OH, one P=O	Tribasic	$P_4O_{10} + 6H_2O (Excess) \longrightarrow 4H_3PO_4$
	2. Peroxomonophosphoric acid	H <sub>3</sub> PO <sub>5</sub> (+5)	Two P—OH, one P=O, one P—O—O—H	Tribasic	$P_4O_{10} + 4H_2O_2 (30\%) + 2H_2O \longrightarrow 4H_3PO_5$
	3. Orthophosphorous acid (Phosphonic acid	H <sub>3</sub> PO <sub>3</sub> (+3)	Two P—OH, one P—H, one P=O	Dibasic	$P_4O_6 + 6H_2O \longrightarrow 4H_3PO_3$
	Hypophosphorous acid (Phosphinic acid)	H <sub>3</sub> PO <sub>2</sub> (+1)	One P—OH, two P—H one P=O	Monobasic	$PCl_3 + 3H_2O \longrightarrow H_3PO_3 + 3HCl$ $2P_4 + 3Ba(OH)_2 + 6H_2O \longrightarrow 2PH_3 + 3Ba(H_2PO_3)_2 + H_2SO_4 \longrightarrow BaSO_4 + 2H_3PO_3$
5	Metaphosphoric acid (exists in polymeric form), e.g.,	HPO <sub>3</sub> (+5)	One P—OH, two P=O	Monobasic	$P_1 + 3NaOH \longrightarrow 3NaHPO + DH + 2HO$
	Cyclotrimetaphosphoric acid	(HPO <sub>3</sub> ) <sub>3</sub> (+5)	Three P—OH, three P=O, three P—O—P	Tribasic	$3H_3PO_3 + 3Br_2 \xrightarrow{\Delta} (HPO_3)_3 + 6HBr$
	Linear polymetaphosphoric acid	(HPO <sub>3</sub> ) <sub>n</sub> (+5)	n(P=O), n(P—OH), n(P—O—P)	Polybasic	$n\mathrm{H_{3}PO_{4}} \xrightarrow{\mathrm{Heat}} \mathrm{HPO_{3}}_{n} + n\mathrm{H_{2}O}$
6.	Pyrophosphoric acid	H <sub>4</sub> P <sub>2</sub> O <sub>7</sub> (+5)	Four O—H, two P=O, one P—O—P	Tetrabasic	$2H_3PO_4 \xrightarrow{523 \text{ K}} H_4P_2O_7 + H_2O$
7.	Peroxodiphosphoric acid	$   H_4 P_2 O_8    (+5) $	Four O—H, two P=O, one P—O—O—P	Tetrabasic	Electrolysis of a mixture of K <sub>2</sub> HPO <sub>4</sub> + KF
	Pyrophosphorous acid	$H_4 P_2 O_5$ (+3)	Two P—OH, two P—H two P=O, one P—O—P	Dibasic	$5H_3PO_3 + PCI_3 \longrightarrow 3H_4P_2O_5 + 3 HCI$
	Hypophosphoric acid	H <sub>4</sub> P <sub>2</sub> O <sub>6</sub> (+4)	Four P—OH, two P=O, one P—P	Tetrabasic	$2P(red) + 4NaOCl + 2H_2O \longrightarrow H_4P_2O_6 + 4NaC$

### ILLUSTRATION 2.13

- a. Why does PCl<sub>3</sub> fume in moisture?
- b. Are all the five bonds in PCl<sub>5</sub> molecule equivalent? Justify your answer.
- c. How do you account for the reducing behaviour of H.PO. on the basis of its structure?
- d. Give the disproportional reaction of H,PO...



a. PCl, hydrolyses in the presence of moisture and gives fumes of HCl.

$$PCl_3 + 3H_2O \longrightarrow H_3PO_3 + 3HCl$$

- b. All 5 bonds are not equivalent.
  - PCl<sub>s</sub> has trigonal bipyramidal geometry, the three P-Cl bonds in the equatorial plane have same bond length and two P-Cl bonds in the axial plane have same bond length. Axial P-Cl bonds are longer than equatorial P-Cl bonds.
- c. In H<sub>3</sub>PO<sub>2</sub>, two H atoms are bonded directly to P atom, hence due to weak P-H bonds H<sub>2</sub>PO<sub>2</sub> acts as a reducing agent.
- **d.** H<sub>3</sub>PO<sub>3</sub> on heating gives H<sub>3</sub>PO<sub>3</sub> and PH<sub>3</sub>.

$$H_3PO_3 \xrightarrow{\Delta} H_3PO_4 + PH_3$$
  
Phosphorous Phosphoric Phosphine acid acid

### CONCEPT APPLICATION EXERCISE 2.1

### Subjective Type

- 1. Write complete balanced reactions for the following:
  - a. Red phosphorous reacts with iodine in presence of water.
  - b. White phosphorous is boiled with a strong solution of NaOH in an inert atmosphere.
  - c. Phosphorous reacts with conc. HNO, to give H,PO,
  - d. Iodine reacts with concentrated nitric acid.
  - e. Orthophosphoric acid is heated with nitric acid and ammonium molybdate.
  - f. Disodium hydrogen phosphate is added to ammonical solution of magnesium sulphate.
  - g. Magnesium is burnt in air and the product is treated with water.
  - h. Phosphine is passed through AgNO<sub>3</sub> solution.
  - i. A mixture of air and ammonia is passed over heated platinum gauze.
  - j. Gold is treated with aqua regia.
  - k. Water is added to calcium phosphide.
  - l. Calcium phosphate is heated with a mixture of sand and carbon.
  - m. Phosphorus reacts with nitric acid to give equimolar ratio of nitric oxide and nitrogen dioxide.
  - n. Zinc is treated with very dilute nitric acid.
  - o. Phosphine is treated with an acidified CuSO<sub>4</sub> solution.

- 2. Describe the action of heat on the following compounds:
  - a. Ammonium nitrate
  - **b.** Ammonium nitrite
  - Ammonium chloride
  - d. Ammonium dichromate
  - e. Orthophosphoric acid
  - f. Phosphrous acid
  - g. Hypophosphorous acid
  - h. Copper nitrate
  - 3. Complete and balance the following reactions:
    - i.  $P_4O_{10} + PCl_5 \longrightarrow$
    - ii.  $NH_3 + NaOC1 \longrightarrow$ \_\_\_\_\_ +  $NaC1 + H_2O$
    - iii.  $Ca(PO_{A})_{3} + 4H_{3}PO_{A} \longrightarrow$
    - iv.  $AgCl + NH_4OH \longrightarrow$ \_\_\_\_\_+
    - v.  $Pb(NO_3)_2 \xrightarrow{\Delta} PbO + \underline{\hspace{1cm}} + \underline{\hspace{1cm}}$
    - vi.  $Mg + HNO_3 \longrightarrow +$
  - 4. In hyponitrous acid, If X is number of  $\sigma$  bonds, Y is the number of non-bonding electrons and Z is the number of  $\pi$  bonds. Then value of  $(X + Y - \frac{Z}{2})$  is
  - 5. If the oxidation state of P in metaphosphate ion, dihydrogen hypophosphite ion and dihydrogen phosphite ion are X, Y and Z respectively. Then value of  $\frac{X+Y+Z}{5}$  is
  - **6.** In cyclotrimetaphosphoric acid (HPO<sub>2</sub>), if X is the number of  $(p\pi - d\pi)$  multiple bonds, Y is the total number of  $sp^3$  – hybridised atoms and Z is number of  $sp^2$  – hybridised atoms. Then value of  $\frac{X+Y-Z}{A}$  is
  - 7. In white or yellow phosphorous, calculate the value of expression  $\frac{P+Q+R+S}{5}$

If P = Atomicity of phosphorous,

Q = Total number of vertex angle in phosphorous molecular

R = Total number of P — P bond in phosphorous.

S = Total number of lone pairs in phosphorous molecule.

# **Solved Examples**

### EXAMPLE 2.1

An aqueous solution of a gas (X) shows the following reactions:

- a. It turns red litmus blue.
- b. When added in excess to a copper sulphate solution, a deep blue coloured solution is obtained.
- c. On addition to FeCl<sub>3</sub> solution, a brownish precipitate is formed, which is soluble in HNO<sub>3</sub>. Identify (X) and give an explanation for step (a), (b)

and (c).

#### Sol. The gas (X) is ammonia, $NH_3$ .

a. Aqueous solution of NH, is NH<sub>4</sub>OH, which is basic and hence turns red litmus blue.

**b.** 
$$CuSO_4 + 4NH_4OH \longrightarrow [Cu(NH_3)_4]^{2+}SO_4^{-2-} + 4H_2O$$
  
Excess Tetraamminecopper(II)
sulphate

[Cu(NH<sub>1</sub>)<sub>4</sub>] SO<sub>4</sub> is deep blue in colour and is soluble in water, hence deep blue coloured solution is formed.

c. 
$$FeCl_3 + 3NH_4OH \longrightarrow Fe(OH)_3 \downarrow + 3NH_4CI$$
Brownish ppt.

$$Fe(OH)_3 + 3HNO_3 \longrightarrow Fe(NO_3)_3 + 3H_2O$$
Soluble

On addition of NH<sub>4</sub>OH to FeCl, solution, brown ppt. of ferric hydroxide, Fe(OH), is formed. Fe(OH), dissolves in HNO, due to formation of ferricnitrate, Fe(NO,),.

### EXAMPLE 2.2

A colourless inorganic salt (A) decomposes completely at about 250°C to give only two products (B) and (C), leaving no residue. The oxide (C) is a liquid at room temperature and neutral to litmus paper while the gas (B) is a neutral oxide. White phosphorus burns in excess of (B) to produce a strong white dehydrating agent. Write balanced equations for the reactions involved in this process.

### Given,

$$(A) \xrightarrow{250^{\circ}C} (B)_{(g)} + (C)_{(l)}$$
Colourless Oxide

inorganic compound

Liquid (C) is neutral oxide at room temperature and neutral to litmus paper.

Gas (B) is neutral oxide.

(B) + 
$$P_4 \longrightarrow$$
 strong white dehydrating agent.

Both (B) and (C) are neutral oxides, (B) helps in combustion of white phosphorous, hence (B) can be nitrous oxide, N<sub>2</sub>O. (C) is liquid at room temperature, hence it can be H<sub>2</sub>O.

$$NH_4NO_3 \longrightarrow N_2O + 2H_2O$$
(A) (B) (C)

$$10N_2O + P_4 \longrightarrow P_4O_{10} + 10N_2$$

P<sub>4</sub>O<sub>10</sub> is strong white dehydrating agent.

(A) is ammonium nitrate, NH<sub>4</sub>NO<sub>3</sub>, (B) is nitrous oxide, N<sub>2</sub>O (C) is water, H<sub>2</sub>O.

#### EXAMPLE 2.3

Identify (A) to (E).

- a. An inorganic iodide (A) on heating with a solution of KOH gives a gas (B) and the solution of a compound (C).
- b. The gas (B) on ignition in air gives a compound (D) and water.
- c. Copper sulphate is reduced to the metal on passing (B) through the solution.
- d. A precipitate of the compound (E) is formed on reaction of (C) with copper sulphate solution.
- Gas (B) on ignition gives water, therefore hydrogen is Sol. present in the gas.

An inorganic iodide with alkali (KOH) gives a gas (R an hydrogen compound, so (A) may be NH<sub>4</sub>I or p<sub>H</sub> As NH<sub>3</sub> does not reduce CuSO<sub>4</sub>, therefore the  $comp_{O(l_h)}$ (A) is  $PH_{\lambda}I$ .

a. 
$$PH_4I + KOH \longrightarrow PH_3 + KI + H_2O$$
(A) (B) (C)

**b.** 
$$4PH_3 + 8O_2 \longrightarrow P_4O_{10} + 6H_2O$$
  
 $P_4O_{10} + 2H_2O \longrightarrow 4HPO_3$   
(D) (Metaphosphoric acid)

c. 
$$3\text{CuSO}_4 + 2\text{PH}_3 \longrightarrow \text{Cu}_3\text{P}_2 + 3\text{H}_2\text{SO}_4$$
  
 $(B)$   
 $\text{Cu}, \text{P}_2 \longrightarrow 6\text{Cu} + \text{P}_4$ 

d. 
$$CuSO_4 + KI \longrightarrow Cu_2I_2 + 2K_2SO_4 + I_2$$
(B) (E)

Hence (A) is  $PH_4I$ , (B) is  $PH_3$ , (C) is  $KI$ , (D) is HPO, and (E) is  $Cu_2I_2$ .

### EXAMPLE 2.4

On gradual addition of KI solution to Bi(NO<sub>3</sub>)<sub>3</sub> solution initially produces a dark brown precipitate which dissolves in excess of KI to give a clear yellow solution. Given an explanation for above observations.

Sol. Bi(NO<sub>3</sub>), undergoes hydrolysis to form HNO<sub>3</sub>.

$$Bi(NO_3)_3 + 3H_2O \longrightarrow Bi(OH)_3 + 3HNO_3$$

HNO, reacts with KI to liberate I,, which dissolves in excess of KI giving clear yellow solution.

$$2HNO_3 \longrightarrow H_2O + 2NO_2 + [O]$$
  
 $2KI + 2HNO_3 + [O] \longrightarrow 2KNO_3 + H_2O + I_2$   
 $I_2 + KI \longrightarrow KI_3$ 

#### EXAMPLE 2.5

- a. A certain element is a metalloid that forms an acidic oxide.  $E_2O_5$ . Identify the element.
- b. N, makes up about 79% of the atmosphere, why do not animals use the more abundant N, instead of O, for the biological processes?
- Sol. a. Since the element forms an oxide with the formula  $E_2O_5$ , it must be an element of group 15. Group 15 has two metalloids namely As and Sb. Acidic character of pentoxides of group 15 decreases down the group Hence As,O<sub>5</sub> is acidic and Sb,O<sub>5</sub> is amphotent Thus the element is As and the metalloid is  $As_2 O_s$ 
  - b. Large amount of energy is needed by the animals for their movement and to maintain the body temperature. Hence, to obtain the energy, it is much easier to break (O=O) bond rather than (N=N) bond, since (O=O) bond is weaker as compared to N≡N bond.

### EXAMPLE 2.6

A translucent white waxy solid (A) on heating in an inert atmosphere is converted into its allotropic form (B). (A) of reaction with very dilute KOH liberates a highly poisonous gas (C), having rotten smell. With excess of chlorine, (C) forms (A) which hydrolyses to compound (E). Identify (A) to (E).

(A) and (B) are allotropes.

$$(A) + KOH \longrightarrow (C)$$

Poisonous gas with rotten smell

$$(C) + Cl_2(Excess) \longrightarrow (D) \xrightarrow{\text{Hydrolysis}} (E)$$
(A) on beging converts into (B) (A)

Since (A) on heating converts into (B), (A) is white phosphorous and (B) is red phosphorous.

$$\begin{array}{ccc}
P_4 & \longrightarrow & P_4 \\
\text{White} & & \text{Red}
\end{array}$$

$$P_4 + 3KOH + 3H_2O \xrightarrow{\Delta} 3KH_2PO_2 + PH_3$$
White

Potassium Phosphine hypophosphite

phosphine (C) is highly poisonous gas.

$$PH_3 + 4Cl_2 \longrightarrow PCl_5 + 3HCl$$
(D)

(D) is phosphorous pentachloride.

$$PCl_s + 4H_2O \longrightarrow H_3PO_4 + 5HCl$$
(E)

(E) is phosphoric acid.

Hence (A) is white phosphorous, (B) is red phosphorous, (C) is phosphine, (D) is phosphorous pentachloride, (E) is phosphoric acid.

### EXAMPLE 2.7

An orange solid (A) on heating gave a green residue (B), a colourless gas (C) and water vapour. The dry gas (C) on passing over heated magnesium gave a white solid (D). (D) on reaction with water gave a gas (E) which formed dense white fumes with HC1. Identify (A) to (E) and give the reactions.

Sol. 
$$(A) \xrightarrow{\Delta} (B) + (C) + H_2O$$
Orange Green Colourless gas

(C) + Mg 
$$\longrightarrow$$
 (D)  $\xrightarrow{\text{H}_2\text{O}}$  (E)  $\xrightarrow{\text{HCl}}$  Dense white fumes.

White gas solid

Since (E) forms dense white fumes with HCl, (E) must be ammonia, NH<sub>3</sub>.

ammonia, 
$$NH_3$$
.  
 $NH_4$  + HCl  $\longrightarrow$   $NH_4$ Cl (Dense white fumes)

 $NH_3$  is formed by hydrolysis of solid (D) hence, (D) is  $Mg_3N_2$ , magnesium nitride.

magnesium nitride.  

$$Mg_3N_2 + 6H_2O \longrightarrow 3Mg(OH)_2 + 2NH_3$$
(E)
(D)
(E)
(E)

Formation of (D) indicates that gas (C) is N<sub>2</sub>.

Thus (A) is ammonium dichromate.

Thus (A) is ammonium dictributed:
$$(NH_4)_2Cr_2O_7 \xrightarrow{\Delta} Cr_2O_3 + N_2 + 4H_2O$$
Orange solid
(A)
(B)
(C)
(C)
(C) is  $N_2$ , (D) is

Hence (A) is  $(NH_4)_2Cr_2O_7$ , (B) is  $Cr_2O_3$ , (C) is  $N_2$ , (D) is  $Mg_3N_2$  and (E) is NH<sub>2</sub>.

# EXAMPLE 2.8

Identify P to V in the following reaction sequence.

(i)  $2 \text{ Pb(NO}_3)_2 \text{ (A)} \longrightarrow 2 \text{PbO} + \text{Brown gas (P)} + O_2(g)$ 

Blue flame colour

(ii) Black ppt 
$$\xrightarrow{\text{dil. HNO}_3}$$
 Pb(NO<sub>3</sub>)<sub>2</sub> + S + H<sub>2</sub>O + Gas (R)

(iii) Gas (P) + Gas (R) 
$$\xrightarrow{\text{Low}}$$
 Blue colour liquid (s)

(V)

Brown Complex

 $FeSO_4 + H_2SO_4$ 
 $T$ 

(iv) Compound (A) + 
$$Na_2CrO_4 \longrightarrow Yellow ppt (V)$$
  
soluble in NaOH

(v) Compound 
$$\textcircled{T} + I^{\ominus} + H^{\oplus} \longrightarrow Gas(R)$$

(i) Gas (P) NO<sub>2</sub>

(ii) Q is Pbs, Gas R is NO.  
(iii) NO<sub>2</sub> (P) + NO (R) 
$$\longrightarrow$$
 N<sub>2</sub>O<sub>3</sub>(S)  

$$Fe_2(SO_4)_3 + 2NO + 4H_2O \xleftarrow{Fe^{+2}H^{\oplus}} 2HNO_2(T)$$

$$FeSO_4 + NO + 5H_2O \longrightarrow [Fe(NO)(H_2O)_5]SO_4$$
Brown Complex
(U)
(iv) Pb(NO<sub>3</sub>)<sub>2</sub> + CrO<sub>4</sub><sup>2</sup>  $\longrightarrow$  PbCrO<sub>4</sub> + NO<sub>3</sub><sup>©</sup>
yellow ppt
(V)
$$PbCrO_4 + 4OH \longrightarrow CrO_4^{2-} + [Pb(OH)_4]^{2-}$$
soluble
(v) NO<sub>2</sub><sup>©</sup>(T) + 2H<sup>©</sup> + I<sup>©</sup>

$$I_2 + NO(R) + H_2O$$

### EXAMPLE 2.9

In the following reactions, If total number of INCORRECT reactions are X, then the value of X is

- (i)  $CuSO_4 + NH_3(aq) \longrightarrow complex is formed$
- (ii)  $CuSO_4 + PH_3 \longrightarrow complex is formed$
- (iii)  $HNO_3 + P_4O_{10} \xrightarrow{\Delta} HPO_3 + N_2O_{10}$
- (iv)  $NH_3 + Cl_2(excess) \xrightarrow{\Delta} NH_4Cl + N_2$
- (v)  $NH_3(excess) + Cl_2 \xrightarrow{\Delta} NCl_3 + HCl$
- (vi)  $NH_3 + NaOCl \longrightarrow N_2H_4 + NaCl + H_2O$
- (vii)  $C_{12}H_{22}O_{11} + HNO_3 \longrightarrow (COOH)_2 + NO_2 + H_2O$
- (viii)  $(NH_4)_2 Cr_2 O_7 \xrightarrow{\Delta} Cr_2 O_3 + N_2 + 4H_2 O_3$
- (ix)  $As_2O_3 + F_2 \longrightarrow AsF_3 + O_2$

### Reaction I, VI, VII and VIII are correct. Sol. Reactions II, III, IV, V & IX are incorrect X = 5

Correct reactions are:

II : 
$$CuSO_4 + PH_3 \longrightarrow Cu_3P_2$$
 (Black ppt.)

III: 
$$CUSO_4 + P_4O_{10} \xrightarrow{\Delta} HPO_3 + N_2O_5$$
  
III:  $HNO_3 + P_4O_{10} \xrightarrow{\Delta} HPO_3 + N_2O_5$ 

III: 
$$HNO_3 + I_4O_{10}$$
  
IV:  $NH_3 + Cl_2(excess) \longrightarrow NCl_3 + HCl_3$ 

$$V : NH_3 + Cl_2 \longrightarrow NH_4Cl + N_2$$

$$V : NH_3(excess) + Cl_2 \longrightarrow NH_4Cl + N_2$$

IX: 
$$AS_2O_3 + F_2 \longrightarrow AsF_5 + O_2$$

### EXAMPLE 2.10

If X is the number of moles required for the thermal decomposition of hypophosphorous acid, then the value of  $(X^2 - 0.5)$  is

#### Sol. (3.5)

$$2H_3PO_2 \xrightarrow{\Delta} H_3PO_4 + PH_3$$
  
 $(X^2 - 0.5) = (2)^2 - 0.5 = 3.5$ 

### EXAMPLE 2.11

Consider the following compounds in their solid state and find the value of (X + Y - Z/2)

where X = Total number of cationic or anionic part is  $sp^3$ 

Y = Total number of compounds having 109°, 28' bond angle either in cationic or anionic part.

Z = Total number of compounds having 90° bond angle either in cationic or anionic part.

### (1.15)

Compound	Solid State
(i) PBr <sub>5</sub>	$[\operatorname{PBr}_4]^{\oplus}\operatorname{Br}^{\ominus}$
	$sp^3$
	(109°, 28')

$$X = 1, Y = 1, Z = 0$$

(ii) 
$$PCl_5$$
  $[PCl_4]^{\oplus}$   $[PCl_6]^{\ominus}$   $sp^3$   $sp^3d^2$   $(109^{\circ}, 28')$   $(90^{\circ})$ 

$$X = 1, Y = 1, Z = 1$$
(iii)  $N_2O_5$ 

$$\begin{array}{ccc}
[\text{NO}_2]^{\oplus} & [\text{NO}_3]^{\ominus} \\
sp & sp^2 \\
(180^\circ) & (120^\circ)
\end{array}$$

$$X = 0, Y = 0, Z = 0$$
  
Total  $X = 1 + 1 + 0 = 2$   
 $Y = 1 + 1 + 0 = 2$ 

$$7 = 0 + 1 + 0 = 1$$

$$Z = 0 + 1 + 0 = 1$$

$$\therefore \left(\frac{X+Y-Z}{2}\right) = \left(\frac{2+2-1}{2}\right) = 1.5$$

#### EXAMPLE 2.12

Consider the following oxyanions:

(ii) 
$$HPO_3^2$$
 (iii)  $H_2PO_2^{\Theta}$ 

(iv) 
$$P_2O_6^{4-}$$

If X = Number of oxyanions having two equivalent P-O bonds per central atoms.

Y = Number of oxyanions having three equivalent P—O bonds per central atoms.

Z = Number of oxy anions having four equivalent P—O bonds per central atom.

Find the value of 
$$2Z - \frac{(X+Y)}{2}$$
.

#### Sol.

Oxyanions	No. of equivalent bonds
O    O    P O O O O O O O O O O O O O O O O O O O	Z=4
(ii) HPO <sub>3</sub> <sup>2</sup> Hydrogen phosphite ion O	<i>Y</i> = 3

Note: PO3-does not exist, Since H.PO, is dibasic

110001103 4000	3 3
(iii) H₂PO₂ <sup>⊖</sup>	X = 2
(Dihydrogen phosphite ion)	
О	
H \ O⊝	
Н	

Note: HPO<sub>2</sub>- and PO<sub>2</sub>- does not exist, since H<sub>2</sub>PO<sub>2</sub> is

	monouasic.	
	$(iv) P_2O_6^{4-}$	Y = 3
	(Hypophosphate ion)	
	ОО	
-	P - P - O =	
	X = 2, Y = 3 + 3 = 6,	7 = 4
-	A - 2, I - 3 + 3 - 6,	Z - 4

$$2Z - \frac{(X+Y)}{2} = 8 - 4 = 4$$

### EXAMPLE 2.13

The following compounds on complete hydrolysis at room temperature gives the products.

- (i) NO. and (ii) NCL Identify the products which acts as:
- a. Dibasic acid
- b. Flexidentate ligand
- c. Both oxidising and reducing agents.
- d. Monodentate ligands
- e. Non redox hydrolysis.

### Sol.

(i) 
$$\stackrel{+4}{NO_2} + \stackrel{+}{H_2}O \xrightarrow{R.T.} \stackrel{+3}{HNO_2} + \stackrel{+5}{HNO_3}$$

**b.,d.**  $NO_2^{\Theta}$  and  $NO_3^{\Theta}$  can act as flexidentate and monodentate ligands.

c. HNO<sub>2</sub> acts as both oxidising and reducing agent.

(ii) 
$$NCl_3 + 3H_2O \xrightarrow{R.T.} NH_3 + 3HOCl$$

- c. HOCl can act as both oxidising and reducing agent.
- d. NH<sub>3</sub> acts as modentate ligand.
- e. It is a non-redox hydrolysis.

# **Exercises**

# Single Correct Answers Type

## physical Properties

- 1. Select incorrect statement
  - (1) Single N—N bond is stronger than P—P bond.
- (2) PH<sub>3</sub> can acts as a ligand in the formation of coordination compound with transition element.
- (3) NO, is paramagnetic in nature.
- (4) Covalency of nitrogen in N<sub>2</sub>O<sub>5</sub> is four.
- 2. Reducing power of 15-group hydrides are in order:
  - (1)  $NH_1 > PH_2 > AsH_3 > SbH_3 > BiH_3$
  - (2)  $BiH_3 > SbH_3 > AsH_3 > PH_3 > NH_3$
  - (3)  $PH_3 > NH_3 > AsH_3 > SbH_3 > BiH_3$
  - (4)  $BiH_3 > SbH_3 > AsH_3 > NH_3 > PH_3$
- 3. The boiling points of the hydrides of 15-group elements are in the order:
  - (1)  $NH_3 > PH_3 > AsH_3 > SbH_3$
  - (2)  $NH_3 > AsH_3 > SbH_3 > PH_3$
  - (3) SbH<sub>3</sub> > NH<sub>3</sub> > AsH<sub>3</sub> > PH<sub>3</sub>
  - (4)  $AsH_3 > SbH_3 > NH_3 > PH_3$
- 4. Elements of group-15 form compounds in +5 oxidation state. However, bismuth forms only one well characterized compound in +5 oxidation state. The compound is
  - $(1) \operatorname{Bi}_2 O_5$

(2) Bi<sub>E5</sub>

(3) Bi<sub>C15</sub>

- (4) Bi<sub>2</sub>S<sub>5</sub>
- 5. In solid state PCl<sub>5</sub> is a ......
  - (1) Covalent solid
  - (2) octahedral structure
  - (3) Ionic solid [PCl<sub>2</sub>]<sup>⊕</sup> octahedral and [PCl<sub>4</sub>]<sup>⊕</sup> tetrahedral
- (4) Ionic solid with [PCl₄]<sup>⊕</sup> tetrahedral and [PCl₆]<sup>⊙</sup> octahedral
- 6. The boiling point of group 15 follows the order.
  - (1) N < P < Bi < Sb < As
- (2)  $P < N < A_S < B_i < S_b$
- (3) N < Bi < P < Sb < As
- (4) P < N < Bi < As < Sb
- 7. Which of the following is the correct order of the thermal stability of hydrides
  - (1)  $NH_3 > PH_2 > AsH_3 > SbH_3 > BiH_3$
  - (2)  $PH_3 > NH_3 > AsH_3 > SbH_3 > BiH_3$
  - (3)  $BiH_3 > SbH_3 > NH_3 > AsH_3 > PH_3$
  - (4)  $NH_3 > BiH_3 > SbH_3 > AsH_3 > PH_3$
- 8. The H M H bond angle of 15 group hydrides decrease from 107° to 90° from NH<sub>3</sub> to SbH<sub>3</sub>; this is due to:
  - (1) increase in strength to bases with molecular weight
  - (2) use of pure p-orbital for M—H bonding in hydrides of higher molecular weight
  - (3) bond energies of M—H bonds increase
- (4) bond pairs of electrons go closer to central atom.

- 9. If X is number of P—O—P bonds in  $P_4O_{10}$  and Y is number of P—I bond in solid  $PI_s$ . Then the value of (X-Y) is
  - (1) 1 (3) 3

- (2) 2(4) 4
- **10.** Boiling / melting points of the following hydrides follow in order
  - (1)  $SbH_3 > AsH_3 > PH_3 < NH_3$
  - (2)  $SbH_3 > AsH_3 > PH_3 > NH_3$
  - (3)  $SbH_{3} > AsH_{3} < PH_{3} < NH_{3}$
  - (4)  $SbH_3 < AsH_3 < PH_3 < NH_3$
- 11. Anomalous behaviour of nitrogen is due to
  - (1) Small size and high EN
  - (2) Non-ability of *d*-orbitals in valence shell
  - (3) Ease of multiple bond formation
  - (4) All
- **12.** The atomicity of phosphorus is X and the P—P—P bond angle is Y. What are X and Y?
  - (1) X = 4,  $Y = 90^{\circ}$
- (2)  $X = 4, Y = 60^{\circ}$
- (3) X = 3,  $Y = 120^{\circ}$
- (4)  $X = 2, Y = 180^{\circ}$
- 13. Nitrogen forms  $N_2$  but phosphorus is converted into  $P_4$  from  $P_2$ . The reason for this is
  - (1) Triple bond is present between phosphorus atoms
  - (2)  $p\pi$ – $p\pi$  bonding is weak
  - (3)  $p\pi$ – $p\pi$  bonding is strong
  - (4) Multiple bond is formed easily
- **14.** The element which forms oxides in all the oxidation states from +1 to +5 is
  - (1) N

(2) P

(3) As

(4) Sb

### Compounds of Nitrogen

- 15.  $p_{\pi} p_{\pi}$  multiple bonding between nitrogen atoms is present in
  - (1) hyponitrous acid
- (2) nitrous acid
- (3) nitric acid
- (4) in all of these
- 16. The nitrogen that decomposes acetylene to cyanogens is
  - (1) Dinitrogen
- (2) Active nitrogen
- (3) Pasive nitrogen
- (4) Both (b) and (c)
- 17. Which of the following statements about N<sub>2</sub>O is false?
  - (1) A neutral oxide which does not form hyponitrous acid with water
  - (2) An oily liquid
  - (3) Used as propellant for whipped ice-cream
  - (4) Used as an anaesthetic
- 18. Nitrogen dioxide:
  - (1) dissolves in water forming HNO,
  - (2) does not dissolve in water
  - (3) dissolves in water to form HNO, and gives off O,
  - (4) dissolves in water to form a mixture of nitrous and nitric acid

#### 2.34 Inorganic Chemistry

- 19. It is recommended that liquor ammonia bottle should be opened after cooling it in ice for sometime. This is because liquor ammonia:
  - (1) brings tears in the eyes
  - (2) is a corrosive liquid
  - (3) is a mild explosive
  - (4) generates high vapour pressure
- 20. It is recommended that liquor ammonia botthe should be opened after cooling it in ice for sometime. This is because liquor ammonia:
  - The principal reducing product is NO gas
  - (II) Cu metal is oxidised to Cu2+ (aq.) ion which is blue in
  - (III) NO is paramagnetic and has one unpaired electron in antibonding molecular orbital
  - (IV) No reacts with O2 to produce NO2 which is linear in shape

Choose the correct statements:

- (1) I, II, III
- (2) I, III

(3) II, IV

- (4) All the above
- 21. A brown ring is formed in the ring test for  $NO_3^{\Theta}$  ion. It is due to the fomation of
  - (1) [Fe(H,O),(NO)]<sup>2+</sup>
- (2) FeSO<sub>4</sub> · NO<sub>2</sub>
- (3)  $[Fe(H_2O)_4(NO)_2]^{2+}$
- (4) FeSO<sub>4</sub> · HNO,
- 22. A black compound of manganese reacts with a halogen acid to give greenish yellow gas. When excess of this gas reacts with NH3 an unstable trihalide is formed. In this process the oxidation state of nitrogen changes from....
  - (1) -3 to +3
- (2) -3 to 0
- (3) -3 to +5
- (4) 0 to -3
- 23. NO<sub>2</sub> is not obtained when following is heated:
  - (1)  $Pb(NO_3)$ ,
- (2) AgNO,

(3) LiNO<sub>3</sub>

- (4) KNO<sub>2</sub>
- 24. Laughing gas is prepared by heating
  - (1) NH<sub>4</sub>Cl+NaNO<sub>3</sub>
- (2) NH<sub>4</sub>Cl
- $(3) (NH_4), SO,$
- (4) NH<sub>4</sub>NO,
- 25. Which blue-liquid is obtained on reacting equimolar amounts of two gases at -30°C?
  - $(1) N_{2}O$

 $(2) N_2O_3$ 

 $(3) N_{2}O_{4}$ 

- (4)  $N_2O_5$
- 26. Which is the correct sequence in the following properties? For the correct order mark (T) and for the incorrect order mark (F):
  - (a) Lewis acidity order:  $SiF_4 < SiCI_4 < SiBr_4 < SiII_4$
  - (b) Melting point: NH<sub>3</sub> > SbH<sub>3</sub> > AsH<sub>3</sub> > PH<sub>3</sub>
  - (c) Boiling point :  $NH_3 > SbH_3 > AsH_3 > PH_3$
  - (d) Bond dipole order :  $NH_3 > SbH_3 > AsH_3 > PH_3$
  - (1) FTFT

(2) TFTF

(3) FFTT

(4) FFTF

- 27. An orange solid (X) on heating gives a colourless gas(y)and only a green residue (Z). Gas (Y) on treatment with  $M_p$ produces a white solid substance:
  - (1) Mg<sub>3</sub>N<sub>2</sub>

(2) MgO

(3) Mg,O,

- (4) MgCl,
- 28. Calcium imide on hydrolysis will give gas (B) which on oxidation by bleaching powder given gas (C). Gas (C) on reaction with magnesium gives compound (D). (D)  $_{0n}$ hydrolysis gives again gas (B). (B), (C) and (D) are:
  - (1) NH<sub>3</sub>, N<sub>2</sub>, Mg<sub>3</sub>N<sub>2</sub>
- (2) N<sub>2</sub>, NH<sub>3</sub>, MgNH
- (3)  $N_2$ ,  $N_2O_5$ ,  $Mg(NO_3)_2$
- (4)  $NH_3$ ,  $NO_2$ ,  $Mg(NO_2)$
- 29. Among the following compounds, which on heating  $d_{0 \text{ heat}}$ produce N,?
  - $(1) (NH_4)_2 Cr_2 O_7$
- (2)  $NH_4C1 + NaNO_3$
- (3)  $NH_{a}C1 + CaO$
- (4)  $Ba(N_3)$ ,
- 30. Nitrogen (I) oxide is produced by:
  - (1) thermal decomposition of sodium nitrite at low temperature
  - (2) thermal decomposition of ammonium nitrite
  - (3) disproportionation of N,O,
  - (4) interaction of hydroxyl amine and nitrous acid
- 31. Match List-I with List-II and select the correct answer using the codes given below the lists:

#### List-II (used in) List-I (Compounds)

- (A) BaSO<sub>4</sub> + ZnS
- (1) Explosive

(B) NI,

- (2) Oxidiser in rocket propellants
- $(C) N_{2}O_{4}$
- (3) Space capsule
- **(D)** KO,
- (4) Pigment
- (A)
- (D) (C) (B)
- ĺ (1) 3
- 2

2

(2) 4

4

- 4 3 2
- (3) 3
- 1
- (4) 4
- 2 1
- 32. Which of the following compound does not product oxyacid of central atom on hydrolysis?
  - (1) BF,

(2) NCl,

(3) SF<sub>4</sub>

- (4) PCl<sub>s</sub>
- 33. The INCORRECT statement regarding 15th group hydride (EH<sub>2</sub>). [E = N, P, As, Sb, Bi]
  - (1)  $NH_3 > PH_3 > AsH_3 > SbH_3 > BiH_3$ : Thermal stability
  - (2) N—H > P—H > As—H > Sb—H > Bi—H :  $E-H^{b00}$ dissociation enthalpy
  - (3)  $NH_3 > PH_3 > AsH_3 > SbH_3 > BiH_3 : Reducing charactors and the second charactors are second contractors.$
  - (4)  $NH_3 > PH_3 > AsH_3 > SbH_3 > BiH_3$ : Basicity
- 34. Which of the following oxyacid contains both P—H # P—P bond simultaneously?
  - $(1) H_{A}P_{2}O_{5}$

(b)  $H_A P_2 O_7$ 

 $(3) H_4 P_2 O_6$ 

(4) None

(2) NO

 $(4) N_{2}O_{5}$ 

- 35. Among the following statement which one is true?
  - (1) NH, is less soluble than PH, in water
  - (2) NH<sub>3</sub> is stronger base and stronger reducing agent than PH<sub>3</sub>
  - (3) NH<sub>3</sub> has higher boiling point than PH<sub>3</sub> and has lower melting point than PH<sub>3</sub>
  - (4) PH<sub>3</sub> is stronger reducing agent than NH<sub>3</sub> and it has lower critical temperature than NH<sub>3</sub>
- **36.** Which of the following statements regarding N<sub>2</sub>O<sub>4</sub> is NOT CORRECT?
  - (1) It is a planar molecule
  - (2) It is used as non-aqueous solvent
  - (3) It involves N—N bond which is larger than the N—N bond in hydrazine
  - (4) Ammonium nitrate in N<sub>2</sub>O<sub>4</sub> acts as a base
- 37. Which of the following on heating produces NO<sub>2</sub>?
  - (1) NaNO<sub>3</sub>

- (2) AgNO<sub>3</sub>
- (3) NH<sub>4</sub>NO<sub>3</sub>
- (4) NH<sub>4</sub>NO<sub>2</sub>
- **38.** Which of the following equation is wrong?
  - (1)  $P_4 + 20HNO_3 \longrightarrow 4H_3PO_4 + 20NO_2 + 4H_2O_3$
  - $(2) I<sub>2</sub> + 10HNO<sub>3</sub> \longrightarrow 2HIO<sub>4</sub> + 10NO<sub>2</sub> + 4H<sub>2</sub>O$
  - (3)  $S + 6HNO_3 \longrightarrow H_2SO_4 + 6NO_2 + 2H_2O_3$
  - (4) None of the above
- 39. Nitrogen gas is liberated by thermal decomposition of:
  - (1) NH<sub>4</sub>NO,

- (2) NaN<sub>3</sub>
- $(3) (NH_4)_2 Cr_2 O_7$
- (4) All
- 40. Two oxides of nitrogen, NO and NO<sub>2</sub> are allowed to react together at 243° K and form a coloured compound of nitrogen (X). When compound (X) reacts with water to yield another compound of nitrogen (Y). The shape of the anion of (Y) molecule is:
  - (1) triangular planar
- (2) triangular pyramidal
- (3) tetrahedron
- (4) square planar
- 41. Consider the following sequence of reaction.

$$Na + NH_3(g) \longrightarrow [X] \xrightarrow{N_2O} [Y] \xrightarrow{Heat} [Z]$$
Gas Pure

Identify [Z] gas:

(1)  $N_2$ 

(2) NH<sub>2</sub>

 $(3) O_{2}$ 

(d) H,

**42.** 
$$NH_3 + O_2 \xrightarrow{Pt} A + H_2O;$$

$$A + O_2 \longrightarrow B$$
;

$$B + O_2 + H_2O \longrightarrow C;$$

A, B and C are:

- (1) N<sub>2</sub>O, NO<sub>2</sub> and HNO<sub>3</sub>
- (2) NO, NO<sub>2</sub> and HNO<sub>3</sub>
- (3) NO<sub>2</sub>, NO and HNO<sub>3</sub>
- (4) N<sub>2</sub>O, NO and HNO<sub>3</sub>
- 43. The mixed anhydride of nitrous and nitric acid is
  - $(1) N_{2}O$

- (2) NO<sub>2</sub>
- (3) NO (4)  $N_2O_5$

(1)  $N_2O_3$  (2)  $N_2O_4$  (3)  $N_2O_5$  (4)  $N_2O$ 

44. Copper reacts with dil. HNO, to form a nitrate and

- **46.** When silver nitrate is heated, the products are (1) Oxygen and metal nitrite
  - (2) Nitrogen dioxide, O<sub>2</sub> and metallic oxide
  - (3) Nitrogen dioxide, O<sub>2</sub> and metal
  - (4) Nitrogen dioxide and metal oxide
- 47. NO is purified by

(1) NO,

 $(3) N_{2}O_{3}$ 

**45.** Nitrogen sequioxide is

- (1) Absorption in (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> solution
- (2) Passing into conc. H, SO<sub>4</sub>
- (3) Absorbing in FeSO<sub>4</sub> solution
- (4) Electrolysis method
- **48.** Which of the following combines with Fe<sup>2+</sup> ions to form brown complex?
  - (1) NO

(2)  $N_2O$ 

 $(3) N_{2}O_{3}$ 

- (4) N,O,
- 49. Nitrogen reacts with calcium and carbon or when N<sub>2</sub> gas is passed over heated calcium carbide (at 1070 K) it gives which is an important fertiliser marketed under the name Nitrolium
  - (1) Calcium nitrate
- (2) Calcium cyanide
- (3) Calcium cvanamide
- (4) Calcium nitride
- **50.** Ordinary strong solution of HCl, HNO<sub>3</sub> and H<sub>2</sub>SO<sub>4</sub> contains roughly
  - (1) 1/5, 2/3 and 3/3 fractions of pure acid and water respectively
  - (2) 2/3, 1/5 and 3/3 fractions of pure acid and water respectively
  - (3) 2/3, 3/3 and 1/5 fractions of pure acid and water respectively
  - (4) None
- **51.** Dilute HNO<sub>3</sub> cannot be concentrated beyond 68% by boiling because
  - (1) On boiling HNO, is decomposed
  - (2) On boiling HNO<sub>3</sub> produces a large amount of heat which is uncontrollable
  - (3) It forms a constant boiling mixture with H<sub>2</sub>O boiling at 394 K
  - (4) It can be concentrated beyond 68% by steam distillation
- **52.** Fuming HNO<sub>3</sub> (containing 98% of HNO<sub>3</sub>) is obtained
  - (1) By distilling 68% HNO<sub>3</sub> with conc. H<sub>2</sub>SO<sub>4</sub>
  - (2) By distilling 68% HNO<sub>3</sub> under reduced pressure
  - (3) By steam distillation of 68% HNO<sub>3</sub>
  - (4) By distillation 68%  $HNO_3$  with  $P_4O_{10}$
- 53. Nitrolim is
  - (1) CaCN,
- (2)  $CaCN_2 + C$

(3) CaC<sub>2</sub>

(4)  $CaCN_2 + CaC_2$ 

2.36 Inorganic Chemistry		Compounds of Phosphorous	
54. Nitrochalk is		Colculate $x + y + z$ for $H_1$	O <sub>3</sub> acid, where x is number of lo
(1) CAN	(2) CaNCN	pairs, y is number of $\sigma$ -bo	onds and 2 is number of $\pi$ -bond <sub>s:</sub>
$(3) (NH_4)_2 SO_4$	(4) Ca(NO <sub>3</sub> ) <sub>2</sub> .CaO	(1) 5	(2) 14
	g acid posses oxidising, reducing and	(3) 13	(4) 12
complex forming prop	(2) HNO,	<b>68.</b> A non-metal $M$ forms $M$ 0	$Cl_3$ , $M_2O_5$ and $Mg_3M_2$ but does $\eta_0$
(1) HNO <sub>3</sub>	(4) HCl		ct statement regarding non-meta
(3) H <sub>2</sub> SO <sub>4</sub> <b>56.</b> Acidic hydride of nitro		M is:	pand
(1) NH <sub>3</sub>	(2) N <sub>3</sub> H	(1) M can form multiple l	
(3) N,H <sub>a</sub>	(4) N,H,	(2) M is of second period	
	lowing pairs is obtained on heating	(3) Atomicity of non-met	
ammonium dichromate	??		n number for $M$ is $+5$ to $-3$
(1) $N_2$ and $H_2O$	(2) $N_2O$ and $H_2O$	<b>69.</b> The formation of $PH_4^{\oplus}$ is $C$	lifficult compared to NH <sub>4</sub> because
(3) NO and H <sub>2</sub> O	(4) NO and NO <sub>2</sub>	(1) lone pair of phosphor	
58. In salt which on heatin	g gives a mixture of two gases is		us resides in almost pure p-orbita
$(1) \text{ NaNO}_3$	(2) KNO <sub>3</sub>	(3) lone pair of phosphor	us resides at $sp^3$ orbital
$(3) Pb(NO_3)_2$	(4) NH <sub>4</sub> NO <sub>3</sub>	(4) lone pair of phosphor	us resides in almost pure s-orbita
	ated with CO <sub>2</sub> under pressure, the		noric acid molecule, how man
product is	(2) NH,CONH,	single and double bonds	
(1) (NH <sub>4</sub> ) <sub>2</sub> CO <sub>3</sub>	(4) NH2EONH2 $(4) NH4HCO3$	(1) 3 double bonds; 9 sing	gle bonds
(3) NH <sub>2</sub> COONH <sub>4</sub>	itric acid which of the following	(2) 6 double bonds; 6 sin	gle bonds
liberates hydrogen?	the acid which of the following	(3) 3 double bonds; 12 si	ngle bonds
(1) Zinc	(2) Copper	(4) Zero double bonds; 12	2 single bonds
(3) Magnesium	(4) Mercury	71. Amongst the following c	ompounds
61. The reaction between N	$NH_2^{\Theta}$ and $N_2O$ gives	$(I)  H_5 P_3 O_{10}$	$H_{6}P_{4}O_{13}$
(1) NO	(2) N2O5	$(III)H_5P_5O_{15}$	$(IV)H_{7}P_{5}O_{16}$
(3) NH <sub>2</sub> NH <sub>2</sub>	(4) N <sub>3</sub> <sup>\to</sup>	non-cyclic phosphates ar	e:
2. Hydrolysis of NCl <sub>3</sub> give	s NH <sub>3</sub> and X. Which of the following	(1) I, III	(2) I, II, III
is X?		(3) I, II, IV	(4) I, II, III, IV
(1) HClO <sub>4</sub>	(2) HClO <sub>3</sub>	72. Strong reducing behavior	ur of H <sub>3</sub> PO, is due to
(3) HOCl	(4) HClO <sub>2</sub>	(1) Low oxidation state of	, <u>-</u>
3. Chlorine reacts with exc		(2) Presence of two –OH	Group and one P—H bonds
(1) NH <sub>4</sub> Cl	(2) N2 + HCl	(3) Presence of one –OH	group and two P—H bonds
(3) $N_2 + NH_4Cl$	(4) $N_2 + NCl_3$	(4) High electron gain en	-
<b>1.</b> In $NO_3^{\Theta}$ ion, the number	per of bond pair and lone pair of	73. The cyclotrimetaphospho	
electrons on nitrogen ato	oms are	(1) (HPO <sub>3</sub> ) <sub>3</sub> and contains	
(1) 2, 2	(2) 3, 1	(2) H <sub>3</sub> P <sub>3</sub> O <sub>6</sub> and contains	
(3) 1, 3	(4) 4, 0	(3) (HPO <sub>3</sub> ) <sub>3</sub> and contains	
<ol><li>A pale blue liquid which mixture of two gases at -</li></ol>	is obtained by reacting equimolar	(4) $H_3P_3O_6$ and contains	
(1) $N_2O_3$	(2) N <sub>2</sub> O	74. Which of the following a	icids forms three series of salts?
(3) $N_2O_4$	(4) $N_2O_5$	(1) H3PO2	(2) H <sub>3</sub> PO,
The INCORRECT order		(3) H <sub>3</sub> PO <sub>4</sub>	(4) H <sub>3</sub> PO <sub>3</sub>
(1) Thermal stability: H		75. $A + H_2O \longrightarrow 6 + HCI$	
		$B + H_2O \longrightarrow C + HC$	
(2) Lewis basic character		Compound (A), (B) and	
(3) % $p$ -character : $NO_2^+$	> NU <sub>3</sub> > NH <sub>4</sub>	(1) PCl <sub>5</sub> , POCl <sub>3</sub> , H <sub>3</sub> PO <sub>3</sub>	(2) $PCl_5$ , $POCl_3$ , $H_3PO_4$
(A) D 1 1 3777 P	TT - A TT		2

(3) SOCl<sub>2</sub>, POCl<sub>3</sub>, H<sub>3</sub>PO<sub>3</sub>

(4) PCl<sub>3</sub>, POCl<sub>3</sub>, H<sub>3</sub>PO<sub>4</sub>

(4) Bond angle :  $NH_3 > PH_3 > AsH_3$ 

- 76. The product formed in the reaction of SOCI, with white phosphorus is:
  - I. PCl,
- II. SO,

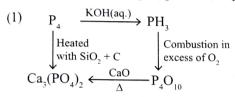
III. S,Cl,

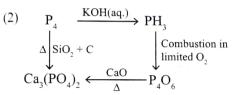
IV. POCl,

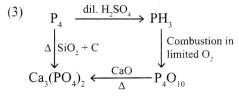
- (1) I, II, III
- (2) II, III, IV

(3) I, II

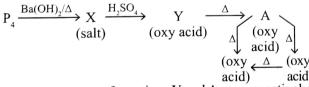
- (4) III, IV
- 77. In which of the following compounds hydrolysis takes place through S<sub>N</sub>1 and S<sub>N</sub>2 mechanism respectively?
  - (1) NF<sub>3</sub>, NCl<sub>3</sub>
- (2) P<sub>4</sub>O<sub>10</sub>, SiCl<sub>4</sub>
   (4) SiCl<sub>4</sub>, SiF<sub>4</sub>
- (3) SF<sub>4</sub>, TeF<sub>6</sub>
- 78. Incorrect statement about PH, is:
  - (1) It is produced by hydrolysis of Ca,P,
  - (2) It gives black ppt. (Cu<sub>s</sub>P<sub>2</sub>) with CuSO<sub>4</sub> solution
  - (3) Spontaneously burns in presence of P<sub>2</sub>H<sub>4</sub>
  - (4) It does not react with B,H,
- 79. Which of the following reacting sequence is correct regarding conversion of phosphorus compounds?







- (4) None of these.
- **80.** Consider the following sequence of reaction:



In the above sequence of reactions Y and A are respectively:

- (1) H<sub>3</sub>PO<sub>2</sub> and H<sub>3</sub>PO<sub>4</sub>
- (2)  $H_3PO_4$  and  $H_3P_2O_7$
- (3) H<sub>2</sub>PO<sub>4</sub> and HPO<sub>3</sub>
- (4) H<sub>2</sub>PO<sub>3</sub> and H<sub>3</sub>PO<sub>4</sub>
- 81. Consider the following reactions:
  - i.  $NH_4C1 \xrightarrow{NaOH} product$  (containing nitrogen)
  - ii. PH<sub>4</sub>I NaOH product (containing phosphorus)
  - iii.  $P_4 \xrightarrow{\text{NaOH}} \text{product (containing phosphorus in negative}$ oxidation state)

The order of change in bond angle (for reactant → specified product) is:

- (1) (i) > (ii) > (iii)
- (2) (ii) > (iii) > (i)
- (3) (iii) > (ii) > (i)
- (4) (ii) > (i) > (iii)

- 82. In which of the following acids, P—P bonds is present?
  - (1) Tetra poly phosphoric acid (H<sub>6</sub>P<sub>4</sub>O<sub>13</sub>)
  - (2) Pyrophosphoric acid (H<sub>2</sub>P<sub>2</sub>O<sub>2</sub>)
  - (3) Hypophosphoric acid (H<sub>4</sub>P<sub>2</sub>O<sub>4</sub>)
  - (4) Polymetaphosphoric acid (HPO<sub>3</sub>)
- 83. Of the following the most acidic is
  - $(1) H_3PO_4$

- (2) H<sub>1</sub>AsO<sub>4</sub>
- (3) H<sub>2</sub>SbO<sub>4</sub>
- (4) H<sub>2</sub>BiO<sub>4</sub>
- 84. Which of the following form maximum P—H bonds.
  - (1) H<sub>3</sub>PO<sub>2</sub>

(2) H<sub>3</sub>PO<sub>4</sub>

(3) H,PO,

- (4) H<sub>4</sub>P<sub>5</sub>O<sub>5</sub>
- **85.** PCl<sub>5</sub> in solid state exists as
  - (1) PCl,

(2) PC1,<sup>⊕</sup>

(3) PCl<sub>c</sub><sup>⊖</sup>

- (4) PCl,<sup>⊕</sup> PCl,<sup>⊝</sup>
- 86. Graham's salt used for softening of water and with other alkalis used for cleaning sinks, drains and floors is
  - (1) (NaPO<sub>2</sub>)
- (2) (KPO<sub>2</sub>)
- (3) Na, PO,
- (4) K, PO,
- 87. The structure of phosphide ion is similar to that of
  - (1) Nitride ion
- (2) Chloride ion
- (3) Fluoride ion
- (4) Sodium ion
- 88. Calcium phosphide is used in smoke screen because it
  - (1) Burns to form soot
  - (2) Gives phosphine which catches fire to give needed smoke
  - (3) Immediately catches fire in air
  - (4) Is a gas which brings tears in the eyes
- 89. Holme's signals produce burning gases which serve as a signal to the approaching ships contains
  - (1) A mixture of Ca,P, and CaC,
  - (2) A mixture of Ca,P, and KOH
  - (3) A mixture of CaC, and KOH
  - (4) A mixture of Ca<sub>2</sub>P<sub>2</sub>, CaC, and KOH
- 90. PCl<sub>3</sub>, P<sub>4</sub>O<sub>6</sub> and P<sub>4</sub>O<sub>10</sub>, PCl<sub>5</sub> on hydrolysis gives respectively
  - (1) H<sub>3</sub>PO<sub>3</sub> and H<sub>3</sub>PO<sub>4</sub>
- (2) H<sub>3</sub>PO<sub>4</sub> and H<sub>3</sub>PO<sub>5</sub>
- (3)  $(HPO_3)_{\mu}$  and  $H_4P_2O_7$  (4)  $H_4P_2O_7$  and  $(HPO_3)_{\mu}$
- 91. The number of P-O-P and P-OH bonds present respectively in pyrophosphoric acid molecule are
  - (1) 2, 3

(2) 1, 8

(3) 1, 4

- (4) 1, 2
- 92. When phosphine is bubbled through a solution of nitrate is precipitated.
  - (1) Silver

- (2) Silver phosphide
- (3) Silver oxide
- (4) None of these
- 93. When orthophosphoric acid is heated at 240°C, the main product formed is
  - (1) H<sub>3</sub>PO<sub>3</sub>

(2) H<sub>2</sub>PO<sub>2</sub>

(3) HPO<sub>3</sub>

(4)  $H_4P_2O_7$ 

- **94.** White phosphorus reacts with caustic soda. The products are PH<sub>3</sub> and NaH<sub>2</sub>PO<sub>2</sub>. This reaction is an example of
  - (1) Oxidation
- (2) Reduction
- (3) Neutralisation
- (4) Disproportionation
- **95.** The number of P—O—P bridges in the structure of  $P_4O_{10}$  and  $P_4O_6$  are respectively
  - (1) 5, 5

(2) 5, 6

(3)6,6

- (4) 6, 5
- **96.** Cl—P—Cl bond angles in PCl<sub>5</sub> molecule are
  - (1) 120° and 90°
- (2) 60° and 90°
- (3) 60° and 120°
- (4) 120° and 30°
- **97.** Scheel's green, formerly used as a green pigment for colouring wall paper is
  - (1) Sodium arsenite (Na<sub>3</sub>AsO<sub>3</sub>)
  - (2) Cupric arsenite (CuHAsO<sub>3</sub>)
  - (3) Silver arsenite (Ag, AsO<sub>3</sub>)
  - (4) None
- 98. Paris green was used as a pigment due to unique light green colour but now-a-days it is used as an insecticide. It is prepared by boiling verdigris (basic acetate of copper). arsenious oxide and acetic acid together. It is
  - (1) (CH<sub>3</sub>COO),Cu·3Cu (AsO,),
  - (2) Cupric acetoarsenite
  - (3) Cu<sub>4</sub> (CH<sub>3</sub>COO), (AsO<sub>2</sub>),
  - (4) All
- 99. Tartar emetic (potassium antimony tartrate) is used as an emetic in small does while larger doses are poisonous. It is used for the treatment of Kala-azar and such other tropical diseases. It is formed when antimonytrioxide (Sb<sub>4</sub>O<sub>6</sub>) is treated with potassium hydrogen tartrate. It is

$$(1) \begin{array}{|c|c|c|c|} \hline CH(OH) COO (SbO) & CH(OH) COO (Sb) \\ \hline (1) & & (2) & & \\ \hline CH(OH) COOK & CH(OH) COOK \\ \hline CH(OH) COO (Sb_2O_3) & CH(OH) COO (SbO_3) \\ \hline (3) & & (4) & \\ \hline CH(OH) COOK & CH(OH) COOK \\ \hline \end{array}$$

100. Which one of the following halide does not hydrolyse?

(1) SbCl<sub>2</sub>

(2) AsCl<sub>3</sub>

(3) PCl,

- (4) NF<sub>2</sub>
- **101.**Wittig reagent is used for the synthesis of alkenes from ketone in organic chemistry. The Wittig reagent is
  - (1)  $(Ph_3P) = CH_2$  Triphenyl phosphine methylene
  - (2)  $(Ph_3P) = O$  Triphenyl phosphine oxide
  - (3) (Ph<sub>3</sub>P) CH<sub>3</sub>Br
  - (4) Ph<sub>3</sub>P
- 102. Following tests are shown by
  - i. Decolourisation of acidified soln. of KMnO<sub>4</sub>
  - ii. Liberation of I, from an acidified soln. of KI
  - iii. On treatment with dil HCl, brown fumes of NO<sub>2</sub> which turns FeSO<sub>4</sub> soln. black

(1) Nitrites

- (2) Nitrates
- (3) Both (a) and (b)
- (4) Neither (a) nor (b)
- 103.PCl<sub>5</sub> exist but NCl<sub>5</sub> does not because
  - (1) NCl, is unstable
  - (2) Nitrogen has no vacant orbitals
  - (3) Nitrogen atom is much smaller
  - (4) Nitrogen is highly inert
- 104.PCl<sub>5</sub> and PH<sub>3</sub> exist but PH<sub>5</sub> does not because
  - (1) PH, is unstable
  - (2) Phosphorous has no vacant orbitals
  - (3) Phosphorous exists as P<sub>4</sub>
  - (4) EN of hydrogen is less as compared to chlorine to excite electron from p orbital to d orbital for bond formation
- 105.N<sub>2</sub> forms NCl<sub>3</sub> whereas P can form both PCl<sub>3</sub> and PCl<sub>5</sub> Why?
  - (1) P has d-orbitals which can be used for bonding but N does not have
  - (2) N atom is larger than P in size
  - (3) P is more reactive towards Cl than N
  - (4) None of the above
- **106.**The following are some statements related to group 15 hydrides
  - i. Reducing property increases from NH<sub>3</sub> to BiH<sub>3</sub>
  - ii. Tendency to donate lone pair decreases from  $\mathrm{NH}_{_{\! 3}}$  to  $\mathrm{BiH}_{_{\! 3}}$
  - iii. Thermal stability of hydrides decreases from  $\operatorname{NH}$  to  $\operatorname{BiH}_3$
  - iv. Bond angle decreases from NH<sub>3</sub> to BiH<sub>3</sub>

The correct statements are:

- (1) (i), (ii), (iii) and (iv)
- (2) (i), (iii) and (iv)
- (3) (i), (ii) and (iv)
- (4) (i) and (iv)
- **107.**Phosphine, acetylene and ammonia can be formed by treating water with
  - (1)  $Mg_3P_3$ ,  $Al_4C_3$ ,  $Li_3N$
- (2)  $Ca_3P_2$ ,  $CaC_2$ ,  $Mg_3N_2$
- (3) Ca<sub>3</sub>P<sub>2</sub>, CaC<sub>2</sub>, CaCN<sub>2</sub>
- (4) Ca,P,, Mg,C, NH, NO,
- **108.**Th  $CN^{\Theta}$  ion and  $N_2$ , are isoelectronic. But in contrast  $^{\mathbb{N}}$   $CN^{\Theta}$ ,  $N_2$  is chemically inert because of
  - (1) Low bond energy
  - (2) Absence of bond polarity
  - (3) Unsymmetrical electron distribution
  - (4) Presence of more number of electrons in bonding orbitals
- 109. White phosphorus on reaction with lime water gives calcium salt of an acid (A) along with a gas (X). Which of the following is correct?
  - (1) (A) on heating gives (X) and O,
  - (2) The bond angle in (X) is less than that in case of ammonia
  - (3) (A) is a dibasic acid
  - (4) (X) is more basic than ammonia

2.39

- (1) One mole of Na<sub>2</sub>HPO<sub>3</sub>
- (2) Two moles of Na,H,PO,
- (3) Two moles of Na<sub>2</sub> HPO<sub>3</sub>
- (4) One mole of Na, PO,
- 111. If O<sub>2</sub> is removed from the formula of anhydride of HNO<sub>2</sub>, then the formula of the resulting compound satisfies which of the following properties?
  - (1) It produces tears in eyes
  - (2) It supports combustion
  - (3) It is paramagnetic
  - (4) It cannot react with red hot copper
- 112. Which of the following statements is correct?
  - (1) N<sub>2</sub>O is a laughing gas and is angular in shape
  - (2) NO<sub>2</sub> is a sweet smelling and is angular in shape
  - (3) NO is a colourless gas and acidic in nature
  - (4) NO<sub>2</sub> on reaction with NaOH gives a mixture of two Salts
- 113. The compound is covalent in gaseous state but ionic in solid state is
  - (1) PCl<sub>5</sub>

(2) PCl,

(3) CCl,

- (4) NH,
- 114. The equivalent mass of phosphoric acid  $(H_3PO_4)$  in reaction, NaOH +  $H_3PO_4 \longrightarrow NaH_2PO_4 + H_2O_7$ , is
  - (1) 29

(2) 49

(3)59

- (4) 98
- 115. The oxyacid of phosphorus in which phosphorus has lowest oxidation state is
  - (1) Hypophosphorus acid
- (2) Orthophosphoric acid
- (3) Pyrophosphoric acid
- (4) Metaphosphoric acid
- 116. Which is/are correct statements about  $P_4O_6$  and  $P_4O_{10}$ :
  - (1) In  $P_4O_6$  each P is joined to three O and in  $P_4O_{10}$  each P is linked to four O atoms.
  - (2) Both (a) and (b) form oxoacids H<sub>3</sub>PO<sub>3</sub> and H<sub>3</sub>PO<sub>4</sub> respectively
  - (3) Both (a) and (b)
  - (4) None
- 117. Blue liquid which is formed at −30°C by mixing of two gases is
  - (1)  $N_2O$

(2)  $N_2O_4$ 

 $(3) N_2O_3$ 

(4)  $N_2O_5$ 

### Multiple Correct Answers Type

### Physical Properties

- 1. Which of the following act as an oxidising as well as a reducing agent?
  - (1)  $HNO_2$

(2)  $H_2O_2$ 

 $(3) H_2S$ 

- (4) SO,
- 2. White phosphorus cannot be separated from red phosphorus by:
  - (1) sublimation
- (2) dissolving in CS,
- (3) distillation
- (4) heating and alkali solution

- 3. Which is true about  $N_2O_5$ ?
  - (1) It is anhydride of HNO,
  - (2) In solid state it exists as NO<sub>2</sub> NO<sub>3</sub>
  - (3) It is structurally similar to  $P_2O_5$
  - (4) It can be prepared by heating HNO<sub>3</sub> over  $P_2O_5$
- **4.** Orthophosphoric acid  $\frac{\text{gentle heat}}{220^{\circ} \text{ C}}$  P

What is/are correct about P?

- (1) It is a tetrabasic acid
- (2) It contains one P O P bond
- (3) It is a dibasic acid
- (4) On hydrolysis it produces metaphosphoric acid
- **5.** At high temperatures, nitrogen directly does not combines with:
  - (1) Zn

(2) Mg

(3) Al

- (4) Fe
- **6.** Which product(s) is not obtained in the following reaction?

$$P + OH \longrightarrow Product(s)$$

(1) PH<sub>3</sub>

(2)  $PO_4^{2-}$ 

 $(3) H_2PO_2^{-}$ 

- (4) PO-,
- 7. Phosphine is not obtained by the reaction when:
  - (1) White phosphorus is heated with NaOH
  - (2) Ca<sub>3</sub>P<sub>2</sub> reacts with water
  - (3) red phosphorus is heated with NaOH
  - (4) phosphorus is heated in current of hydrogen
- 8. Which of the following statements is/are incorrect?
  - (1) NO, is a diamagnetic substance
  - (2) Solid is brown in colour
  - (3) NO, dimerizes to N<sub>2</sub>O<sub>4</sub>
  - (4) NO<sub>2</sub> is a mixed anhydride
- 9. Which of the following statements are true about  $P_4O_8$  and  $P_4O_{10}$ ?
  - (1) Both these oxides have a closed cage like structure
  - (2) Each oxide requires 6 water molecules for complete hydrolysis to form their respective oxoacids
  - (3) Both these oxides contain 12 equivalent P—O bonds
  - (4)  $P_4O_6$  and  $P_4O_{10}$  both contains  $p\pi-d\pi$  bonds
- **10.** Which of the following, when dissolved in water, will liberated ammonia?
  - (1) NaNO,

- (2) NaNO,
- (3) NaNH,
- (4) Na<sub>3</sub>N<sub>2</sub>
- 11. Which of the following is not true for allotropes or phosphorus?
  - (1) Yellow phosphorus is soluble in CS<sub>2</sub> while red phosphorus is not
  - (2) P P P bond angle is 60° in red phosphorus
  - (3) On heating in air, white phosphorus changes to red
  - (4) White phosphorus slowly changes to red phosphorus at ordinary temperatures

### 2.40 Inorganic Chemistry

- 12. PH, can be obtained by:
  - (1) heating hypophosphorus acid
  - (2) heating orthophosphorus acid
  - (3) reaction of P<sub>4</sub> with hot conc. NaOH
  - (4) hydrolysis of calcium phosphide
- 13. Select the correct trends.
  - (1) N < P < Bi < Sb < As (Melting point)
  - (2) N > P > As > Sb > Bi (Ionisation energy)
  - (3) N > P > As > Sb > Bi (Electronegativity)
  - (4) P < N < As < Bi < Sb (Melting point)
- 14. Which of the following statements are INCORRECT?
  - (1) The number of P O P bond in  $P_4O_6$ ,  $P_4O_8$  and  $P_4O_{10}$  are equal in number.
  - (2)  $P_4O_8$  and  $P_4O_{10}$  have 5 P O P bonds
  - (3)  $P_4O_{10}$  has 4 '— P = O'
  - (4)  $P_4O_6$  and  $P_4O_8$  have zero and two -P=O bonds respectively.
- 15. Which of the following orders are correct according to indicated property
  - (1)  $N_2O < NO < N_2O_3 < N_2O_4 < N_2O_5$  (strength of oxides of nitrogen)
  - (2)  $P_4O_6$  and  $N_2O_3$  <  $As_4O_6$  >  $Sb_4O_6$  (acidic strength of trioxides)
  - (3)  $N_2O_5 > P_4O_{10} > As_4O_{10} > Sb_4O_6$  (acidic strength of pentoxides)
  - (4)  $Pl_3 < PBr_3 > PCl_3 > PF_3$  (Bond angle)
- 16. Choose the correct statements
  - (1)  $NF_3 < NCl_3 < NBr_3 < NI_3$  (Lewis base strength)
  - (2) In hydrolysis of SbCl<sub>3</sub>, the addition of excess of HCl suppresses the hydrolysis by shifting the equilibrium to the left
  - (3) NF<sub>3</sub> does not undergo hydrolysis
  - (4) Thermal stability of PCl<sub>3</sub> > PCl<sub>5</sub>
- 17. Which of the following statements are incorrect?
  - (1) All the three N O bond length in HNO $_3$  are equal
  - (2) All P C bond length in PCl<sub>5</sub> molecule in gaseous state are equal
  - (3) P<sub>4</sub> molecule in white phosphorus have angular strain therefore white phosphorus is very reactive
  - (4) PCl<sub>5</sub> is ionic in solid state in which cation is octahedral and anion tetrahedral

### Compounds of Nitrogen

- 18. Which of the following compounds is NOT obtained when  ${\rm HNO_3}$  reacts with  ${\rm P_4O_{10}}$ .
  - $(1) N_2O_5$

(2) NO<sub>2</sub>

(3) NO

- (4) HPO<sub>3</sub>
- 19. Which of the following compound(s) are explosive(s)?
  - (1) NCl,

(2) Nl,

(3) NBr<sub>3</sub>

(4) NF<sub>3</sub>

- 20. The following side reaction in the production of  $N_2H_4$   $N_2H_4 + 2NH_4Cl \longrightarrow N_2 + 2NH_4Cl$ 
  - (1) is catalysed by traces of heavy metals as Cu2+
  - (2) is suppressed by addition of geletin or glue
  - (3) is made reversible by removing  $N_2$
  - (4) is made reversible by adding NaOH
- 21. The nitrogen oxide(s) that contain (s) N—N bond(s) is (a<sub>loc</sub>)
  - $(1) N_{2}O$

(2)  $N_2O_3$ 

 $(3) N_{2}O_{4}$ 

- (4)  $N_2O_5$
- 22.  $N_2H_4$  reduces  $IO_3^{\Theta}/H^{\oplus}$ 
  - (1) to I<sup>⊕</sup>
  - (2) with  $I_2$  as an intermediate indicated by violet colour in  $C_0$  layer
  - (3) indicated by blue colour with starch
  - (4) to  $I^{\odot}$
- 23. Ammonia reacts with Nessler's reagents to give a brown ppt. due to formation of
  - (1)  $H_2N Hg O Hgl$
- (2) IO<sub>3</sub><sup>⊖</sup>
- (3) Iodide of Millon's base
- (4) K<sub>2</sub> Hg I<sub>4</sub>
- 24. Which of the following are used as fertilizers?
  - (1)  $Ca_3(PO_4)_2$
- (2)  $Ca(H_2PO_4)_2$

(3) CaNCN

- (4) CaC<sub>2</sub>
- 25. Photochemical decomposition of HNO<sub>3</sub> produces:
  - (1)  $N_2$

(2)  $N_2O$ 

(3) NO<sub>2</sub>

- (4) O,
- 26. Which of the following statement(s) regarding nitrogen sesquioxide (N<sub>2</sub>O<sub>3</sub>) is/are correct?
  - (1) Nitrogen sesquioxide is stable only in the liquid state

    It dissociates in the vapour state
  - (2) Nitrogen sesquioxide is a neutral oxide
  - (3) Nitrogen sesquioxide contains a weak N N bond
  - (4) Nitrogen sesquioxide exists in two different forms
- 27. Select the correct reaction(s)
  - (1)  $NH_4NO_3 \xrightarrow{250 \text{ °C}} N_2O + 2H_2O$
  - (2)  $NH_2OH + HNO, \xrightarrow{\Delta} N, O + 2H, O$
  - (3)  $4NH_3 + 5O_2 \xrightarrow{Pt} 4NO + 6H_5O_2$
  - (4)  $As_2O_3 + HNO_3(dil) \longrightarrow N_2O_3 + 2H_3AsO_4$
- 28. The metals which produce hydrogen only with very diluteration acid are
  - (1) Zn

(2) Cu

(3) Mg

- (4) Mn
- **29.** The nitrogen oxide(s) that contain(s) N N bond(s) is( $\mathfrak{g}^{(n)}$ )
  - (1)  $N_2O$

 $(2) N_{2}O_{3}$ 

 $(3) N_{2}O_{4}$ 

- $(4) N_2O_5$
- 30. A solution of colourless salt on boiling with excess NaO produces a non-flammable gas. The gas evolution cease after sometime upon addition of Zn dust to the same solution the gas evolution restarts. The colourless salt(s) is (are)

- (1) NH<sub>4</sub>NO<sub>3</sub>
- (2) NH<sub>4</sub>NO,

- (3) NH<sub>4</sub>Cl
- $(4) (NH_4)_2SO_4$

# Compounds of Phosphorous

- 31. Which of the following are similarities between  $H_4P_4O_{12}$  and  $H_4P_2O_7$ ?
  - (1) Structure
  - (2) Total number of atoms directly bonded by reach phosphorous atom
  - (3) Type of linkage (X-O-X/X-X)
  - (4) Number of P O P linkage
- 32. PCl, is formed when:
  - (1) white phosphorus reacts with limited dry chlorine
  - (2) white phosphorous reacts with excess of dry chlorine
  - (3) white phosphorus reacts with excess of SO<sub>2</sub>Cl<sub>2</sub>
  - (4) white phosphorus reacts with excess of SO,Cl,
- 33. Which of the following is incorrect for P<sub>4</sub> molecule of white phosphorus?
  - (1) It has 6 lone pairs of electron
  - (2) It has 6 P—P single bonds
  - (3) It has 3 P—P single bonds
  - (4) It has 4 lone pairs of electrons
- 34. Which of the following statements are incorrect?
  - (1) In phosphorous acids, formal oxidation state of P is +1 and +3
  - (2) In phosphoric acids, formal oxidation state of P is +5.
  - (3) The oxoacids in +3 oxidation state undergo disproportionation reaction to give compounds in lower and higher oxidation states.
  - (4) H<sub>3</sub>PO<sub>3</sub> is stronger reducing agent than H<sub>3</sub>PO<sub>2</sub>.
- 35. Consider the following reactions:

$$X_x + Yy_2 \xrightarrow{\text{Limited}} \text{Compound} \xrightarrow{\text{excess}} \text{Compound}$$
(A)  $\xrightarrow{\text{excess}}$  (B)

(Atomic number of element X and Y are 15 and 8)

Select the correct statements:

- (1) (Y-X-Y) bond angle in B > (Y-X-Y) bond angle in A.
- (2) (X-Y) bond length in  $B \le (X-Y)$  bond length in A.
- (3) Compound A is  $P_2O_5$  and compound B is  $P_4O_{10}$
- (4) Value of X + Y + Z = 9
- **36.** Consider the following reactions:
  - (i) Hydrolysis of one mole of calcium phosphide
  - (ii) Reaction of KOH with 1 mole of white P<sub>4</sub>.
  - If X is the number of moles of H<sub>2</sub>O in reaction (i) and Y is the number of P—H bonds in the products of reaction (ii).
  - Select the correct statements
  - (1) PH<sub>3</sub> is formed in both reactions
  - (2)  $H_2PO_2^{\odot}$  is formed in reaction (i)
  - (3) The value of Y is 5.
  - (4) The value of X Y = 1.

- 37. What is/are not true about phosphine (PH<sub>1</sub>)?
  - (1) It turns red litmus blue.
  - (2) It reacts with HCl(aq.) to give PH<sub>2</sub>Cl
  - (3) Phosphonium compounds are obtained when anhydrous phosphine reacts with anhydrous halogen acids.
  - (4) It is prepared by hydrolysis of metal phosphides with acids.
- 38. Which of the following reactions can evolve phosphine?
  - (1) White  $P + Ca(OH)_2 \longrightarrow$
  - (2) AlP +  $H_2O \longrightarrow$
  - $(3) H_3PO_4 \xrightarrow{\text{Heat}}$
  - (4)  $PH_4I + NaOH \longrightarrow$

### **Linked Comprehension Type**

### Paragraph 1

NH<sub>3</sub> has got pyramidal structure. By replacement of H atoms it forms (CH<sub>3</sub>)<sub>3</sub>N and (SiH<sub>3</sub>)<sub>3</sub>N molecules which are found to have different geometries.

- 1. Which is the correct relation of bond angles?
  - (1)  $NH_3 > (CH_3)_3 N > (SiH_3)_3 N$
  - (2)  $(SiH_3)_3N > (CH_3)_3N > NH_3$
  - (3)  $NH_3 > (SiH_3)_3 N > (CH_3)_3 N$
  - (4)  $(CH_3)_3N > (SiH_3)_3N > NH_3$
- 2. Shape of (SiH<sub>3</sub>)<sub>3</sub>N with respect to N is
  - (1) Pyramidal
- (2) T-shaped
- (3) Trigonal planar
- (4) Tetrahedral
- 3. Which of the following has highest basic character?
  - (1) NH,

- (2) (CH<sub>2</sub>),NH
- $(3) (CH_3)_3 N$
- (4) (SiH,),N

#### Paragraph 2

Solid  $N_2O_5$  exists as  $NO_2^{\oplus}NO_3^{\odot}$  and hence is called nitronium nitrate.

- 4. The gas which is acidic in nature is
  - (1) NO

(2) N,O

(3) NO,

- (4) Both (a) and (b)
- **5.** Which of the following statement is correct for the oxides of nitrogen?
  - (1) Dinitrogen trioxide dissolves in potassium hydroxide forming potassium nitrate.
  - (2) Aqueous solution of nitrogen dioxide behaves both as a reducing agent and as an oxidising agent.
  - (3) NO, is non-planar.
  - (4) Nitrous oxide is fairly soluble in cold water and turns blue litmus red.
- 6. Choose the incorrect statement:
  - (1) NO<sub>2</sub> molecule is angular with N-O distance equal to intermediate distance between a single and a double bond.
  - (2) In N<sub>2</sub>O<sub>4</sub> the N-N bond length is longer than the usual N-N single bond distance.
  - (3) N<sub>2</sub>O is a linear molecule and has a small dipole moment.
  - (4) None of these

### Paragraph 3

PCl<sub>s</sub> has trigonal pyramidal geometry with sp<sup>3</sup>d hybridisation in gases and liquid state but in solid state it exist as ionic compound.

- 7. The hybridisation of P and shape of POCl, are
  - (1)  $sp^3$ , tetrahedral
- (2)  $sp^3d$ , distorted tetrahedral
- (3)  $sp^3d$ , square planar
- (4)  $sp^3$ , pyramidal
- 8. In presence of small amount of water, PCl, hydrolyses to form
  - (1) PCl,

- (2) H,PO,
- (3) POCI,
- (4) POC1
- 9. In crystalline state PCl<sub>5</sub> exists as
  - (1)  $[PCl_{3}]^{2+} + 2Cl^{\Theta}$
- (2)  $[PCl_{\lambda}]^{\oplus} [PCl_{\lambda}]^{\Theta}$
- (3) [PCl,]<sup>⊕</sup>Cl<sup>⊙</sup>
- (4)  $[PCl_4]^{\oplus} [PCl_4]^{\Theta}$
- 10. What is the hybridisation state of cation part of solid PCl,?
  - (1)  $sp^3d^2$

(2)  $sp^3d$ 

(3)  $sp^3$ 

(4)  $sp^2$ 

### Paragraph 4

The pronounced change from non-metallic to metallic behaviour and also increase in the basicity of oxides from nitrogen to bismuth in group 15 is principally due to increasing size of the atoms. The ionisation potential of nitrogen is very high on account of its small size. However, ionisation potential decreases regularly on descending the group.

- 11. Which one of the following is a strongest base?
  - PH,

(2) SbH,

(3) AsH,

- (4) NH<sub>2</sub>
- 12. Among the trihalides of nitrogen, which one is least basic?
  - (1) NF<sub>3</sub>

(2) NI<sub>3</sub>

(3) NBr,

- (4) NCl,
- 13. Which one of the following fluorides does not exist?
  - (1) NF,

(2) SbF<sub>5</sub>

(3) AsF,

- (4) PF<sub>5</sub>
- 14. Which of the following oxides is most acidic?
  - (1) Bi<sub>2</sub>O<sub>3</sub>

(2)  $P_{2}O_{3}$ 

(3) As<sub>2</sub>O<sub>3</sub>

- (4) Sb<sub>2</sub>O<sub>3</sub>
- 15. The most unstable hydride is
  - (1) NH<sub>3</sub>

(2) SbH<sub>3</sub>

(3) BiH,

- (4) PH<sub>2</sub>
- 16. In all the group 15 elements, the number of unpaired electrons in the valence shell is
  - (1) 2

(2) 3

(3) 4

- (4) 5
- 17. Which trihalide is most ionic among the following?
  - (1) NCl<sub>3</sub>

(2) PCl<sub>1</sub>

(3) BiF<sub>3</sub>

(4) SbF<sub>3</sub>

#### Paragraph 5

Phosphorus forms a number of oxoacids which differ in their structures and oxidation state of phosphorus. All the acids contain phosphorus atom/atoms linked tetrahedrally to four

other atoms or groups. Each of them has at least one P=0 other atoms of groups. Experimentally of the physical points of the physical physic H atom linked directly to P is non-ionisable. Structures of all the acids are considered to be derived either from phosphorus acids or phosphoric acid.

- 18. Which one is monobasic acid?
  - (1) H<sub>3</sub>PO<sub>2</sub>
- (2) H,PO,
- (3) H,PO<sub>4</sub>
- (4) H,PO,
- 19. Which one has +3 oxidation state?
  - $(1) H_3PO_4$
- (2) H<sub>2</sub>PO,
- (3) H<sub>4</sub>P<sub>2</sub>O<sub>7</sub>
- (4) H<sub>4</sub>P<sub>5</sub>O<sub>5</sub>
- 20. The acid which forms two series of salts is
  - (1) H,PO,
- (2) H<sub>2</sub>PO<sub>2</sub>

(3) HPO<sub>3</sub>

- (4) H,PO,
- 21. Which of the following is a cyclic oxoacid?
  - $(1) H_4P_2O_7$
- (2)  $H_4P_2O_6$ (4)  $H_5P_5O_{15}$
- (3) H<sub>4</sub>P<sub>5</sub>O<sub>0</sub>
- 22. The number of or P=O and P-O-H bonds in H<sub>2</sub>PO<sub>dre</sub>
  - (1) 3, 1

(2) 2, 2

(3) 1, 2

(4) 1, 3

### Matrix Match Type

This section contains questions each with two columns-I and II Match the items given in column I with that in column-II.

1.		Column I		Column II
	(1)	Superphosphate of lime	p.	N <sub>2</sub> O
	(2)	Laughing gas	q.	N <sub>2</sub>
	(3)	Inert gas	r.	NH <sub>4</sub> Cl
	(4)	Sal ammoniac	s.	Ca(H <sub>2</sub> PO <sub>4</sub> ) <sub>2</sub> ·H <sub>2</sub> O·2CaSO <sub>4</sub> · 2H <sub>2</sub> 0

2.		Column I		Column II
	(1)	Anhydride of HNO <sub>3</sub>	p.	Phosphorous trioxide
	(2)	Anhydride of HNO <sub>2</sub>	q.	Phosphorous pentoxide
	(3)	Anhydride of HPO <sub>3</sub>	r.	Nitrogen pentoxide
	(4)	Anhydride of H <sub>3</sub> PO <sub>3</sub>	s.	Nitrogen trioxide

3.	1	Mixture		Solution used for seperation
	(1)	PH <sub>3</sub> and NH <sub>3</sub>	p.	H <sub>2</sub> SO <sub>4</sub>
	(2)	N <sub>2</sub> and NH <sub>3</sub>	q.	Ammoniacal CuCl
	(3)	N <sub>2</sub> and Co	r,	Water
	(4)	N <sub>2</sub> and O <sub>2</sub>	s.	Pyrogallol

4.	34.57	Column I		Column II
	(1)	Dibasic acid	p.	Phosphorous acid
	(2)	Tribasic acid	q.	Ammonium nitrate
	(3)	Monobasic acid	r.	Orthophosphoric acid
	(4)	Freezing salt	s.	Hypophosphorous acid

		Column I	1	Column II
(	1)	Acid hydride of N	p.	Nitrogen dioxide
1	2)	Basic hydride of N	q.	Ammonia
(:	3)	Brown coloured gas	r.	Hydrazoic acid
(4	4)	Colourless gas	s.	Nitric oxide
		Column I		Column II
(1	)	Salammoniac	p.	Ammonia
(2	)	Haber process	q.	Ammonium chloride
(3	)	Ostwald's process	r.	NH <sub>4</sub> NO <sub>3</sub> + CaCO <sub>3</sub>
(4	)	Nitrochalk	s.	Nitric acid
	1	Column I	11:10	Column II
(1)	1	Hypophosphorous acid	p.	$H_4P_2O_7$
(2)	F	Phosphorous acid	q.	H <sub>3</sub> PO <sub>4</sub>
(3)	F	Phosphoric acid	r.	$H_3PO_3$
(4)	P	yrophosphoric acid	s.	H <sub>3</sub> PO <sub>2</sub>
1 形	C	Column I (Reactions)		Column II (Products)
1)	1	Ig and Pb with dil NO <sub>3</sub>	p.	Metal nitrates + H <sub>2</sub>

	Column I	1014	Column II
(4)	Mg, Mn and Ca with dil. HNO <sub>3</sub>	S.	Metal nitrates + N <sub>2</sub> C
(3)	Zn, Fe and Sn with dil. $HNO_3$	r.	Metal nitrates + NO
(2)	Zn, Fe and Sn with very dil. HNO <sub>3</sub>	q.	Metal nitrates + NH <sub>2</sub> OH or NH <sub>4</sub> NO <sub>3</sub>

	Column I (Reactions)		Column II (Products)
(1)	Cu, Ag, Hg, Pb and Zn with conc. HNO <sub>3</sub>	p.	H <sub>2</sub> SnO <sub>3</sub> and NO <sub>2</sub>
(2)	Fe with moderately conc. HNO <sub>3</sub>	q.	Metal nitrates + NO
(3)	Fe, Al, Co, Ni and Cr with conc. HNO <sub>3</sub>	r.	Ferric nitrate + NO
(4)	Sn with conc. HNO <sub>3</sub>	s.	Rendered passive

	Column I	The state of	Column II
(1)	Phosphorite	p.	3Ca <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub> CaCl <sub>2</sub>
(2)	Chloroapatite	q.	3Ca <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub> CaF <sub>2</sub>
(3)	Fluoroapatite	r.	CAN
(4)	Nitrochalk	s.	$Ca_3(PO_4)_2$

11. Match the items given in Column I with that in Column II and III

Column I Column II

	Column I		Column II		Column III
	Oxides of		Method of preparation		Characteristics
(1)	nitrogen N <sub>2</sub> O	i.	Pb $(NO_3)_2$ $\xrightarrow{\Delta}$ 2PbO + $O_2$ + LiNO <sub>3</sub> and Mg $(NO_3)_2$ , also give same reaction.	p.	Colourless, neutral gas. On heating at $600^{\circ}$ C, gives $N_2 + O_2$
(2)	NO	ii.	$LINO_3$ and $Mg$ ( $NO_3/_2$ , also $green$ ) $4AgNO_3 + 2Cl_2 \longrightarrow 4AgCl + O_2 + \dots$	q.	Colourless gas, in solid and liquid state it is blue in colour. On heating at 1100°C, gives N <sub>2</sub> + O <sub>2</sub>
(3)	NO <sub>2</sub>	iii.	$NH_4NO_3 \xrightarrow{\Delta} \dots + 2H_2O$	r.	It is an hydride of HNO <sub>3</sub> and acidic in nature. In solid state, it exists as: $[NO_2]^{\oplus} [NO_3]^{\ominus}$
(4)	N <sub>2</sub> O <sub>5</sub>	iv.	Catalytic oxidation of NH <sub>3</sub> . $4NH_3 + 5O_2 \xrightarrow{Pt} \dots + 6H_2O$	s.	Brown gas highly reactive and paramagnetic Acts as an oxidising agent.

Match the items given in Column I with that in Column II and III

. Matc	h the items given in Column I with the	at III	Column II		Column III
	Column I				Main products
	Different concentration of HNO <sub>3</sub>		Elements	1/19	Complex ions + NO(g)
		i.	Fe, Al, CO, Ni, and Cr		
(1)	Conc. HNO <sub>3</sub>	ii.	Cu, Ag, Hg, Pb and Zn		Rendered passive
(2)	Dil. HNO <sub>3</sub>			r.	Metal nitrates + NO(g)
	3 22 - 보고 :	10.39	Noble metals like Au, Pt		Metal nitrates + NO <sub>2</sub> (g)
(3)	Cold dil. HNO <sub>3</sub>	iv.	Cu, Ag, Hg and Pb	S.	Metal infraces + H (g)
(4)	Aqua regia		Mg and Mn	t.	Metal nitrates + H <sub>2</sub> (g)
(4)		V.	Mg and win		
1 24					

### For Q. 13 to Q. 16:

Answer the questions given below by appropriately matching the information given in three Column of the following table.

	E.C. of 15 group elements		Characteristics (I)		Characteristics (II)
(1)	$6s^2 6p^3$	i.	Metalloid	p.	Least stable hydride.
(2)	$3s^2 3p^3$	ii.	Basic oxides and metallic in character	q.	Exists in tetrahedra tetra-atomic forms and are solid
(3)	4s <sup>2</sup> 4p <sup>3</sup>	iii.	Its hydride have highest bond angle amongst other hydrides	r.	Do not form sulphides
(4)	$2s^2 2p^3$	iv.	Grahm salt	s.	Shows inert pair effect

- 13. For the element nitrogen, CORRECT combination is:
  - (1) b—iv—q
- (2) b—iv—q,s
- (3) d—iii—r
- (4) d—iv—q,s
- 14. For the element phosphorous, CORRECT combination is:
  - (1) b—iv—q
- (2) b—iv—q,s
- (3) d—iii—r
- (4) d—iv—q,s
- 15. For the element arsenic, CORRECT combination is:
  - (1) b—iv—q,s
- (2) b—iv—s
- (3) c—i—q
- (4) c—i—q,s
- 16. For the element bismuth, CORRECT combination is:
  - (1) a—ii—p,q,s
- (2) a—ii—p,q
- (3) a—ii—p
- (4) a—i—p,q,s

### Numerical Value Type

- 1. How many nitrogen oxides are known?
- 2. How many lone pairs are present in nitrogen molecule?
- 3. In group 15 elements, the number of unpaired electrons in valence shell is \_\_\_\_\_\_.
- 4. How many P-O-P bonds are present in P<sub>4</sub>O<sub>8</sub>?
- 5. In solid PCl<sub>5</sub> molecule, how many P-Cl bonds are present in the cation?
- **6.** What is the basicity of pyrophosphoric acid?
- 7. How many  $\sigma$ -bonds are present in  $N_2O_3$ ?
- **8.** When excess of ammonia and chlorine react, nitrogen and ammonium chloride are formed. Write the balanced equation and find out how many ammonium chloride molecules are involved in the balanced equation?
- **9.** What is the atomicity of phosphorous?
- **10.** How many N—O ( $\sigma$ ) bonds are present in N<sub>2</sub>O<sub>5</sub>?
- 11. In P<sub>4</sub>O<sub>10</sub>, how many oxygen atoms are bonded to each phosphorous atoms?
- 12. How many unpaired electrons are present in NO molecule?
- **13.** The number of vacant orbitals in the valence shell of phosphorous is
- **14.** How many hydrogen bonds are formed by each H<sub>3</sub>PO<sub>4</sub> molecule?
- **15.** On hydrolysis, of calcium phosphide, how many moles of phosphine are formed?

- 16. How many lone pairs are present in white phosphorous?
- 17. How many bridging oxygen atoms are present in P<sub>4</sub>O<sub>1.2</sub>?
- 18. How many moles of H<sub>3</sub>PO<sub>4</sub> are obtained on hydrolysis one mole of P<sub>4</sub>O<sub>8</sub>.
- 19. On hydrolysis of magnesium nitride, how many moles of ammonia are produced?
- 20. How many electrons are present in the valence shell of P in PCl<sub>3</sub>?
- 21. The following oxides of nitrogen are given:
  - (i) N<sub>2</sub>O
- (ii) NO
- (iii) N<sub>2</sub>O<sub>2</sub>

- (iv) NO,
- $(v) N_2O_4$
- (vi)  $N_2O_2$

If X is the number of neutral oxide and Y is the number of paramagnetic oxide then find the value of  $\frac{(X+Y)^2}{5}$ 

- **22.** In the following compounds
  - (i)  $P_4O_{10}$
- (ii) Solid PI,

Calculate the value of  $\left(\frac{X+Y}{6}\right)$ .

If X is the total number of  $sp^3$  hybridised atoms in both  $ab_{0}v_{0}$  compounds Y is the total number of  $sp^2$  hybridised atoms in both above compounds.

### **Archives**

#### JEE MAIN

### Single Correct Answer Type

- 1. Which one of the following properties is not shown by NO?
  - (1) It is diamagnetic in gaseous state
  - (2) It is a neutral oxide
  - (3) It combines with oxygen to form nitrogen dioxide
  - (4) Its bond order is 2.5
- (JEE Main 2013)
- 2. Which of the following statements is wrong?
  - (1) The stability of hydrides increases from NH<sub>3</sub> to BiH<sub>3</sub> in group 15 of the periodic table
  - (2) Nitrogen can't form  $d\pi p\pi$  bond
  - (3) Single N—N bond is weaker than the single P—P bond
  - (4)  $N_2O_4$  has two resonance structure.
- (JEE Main 2014)
- Statement I: Nitrogen and Oxygen are the main components in the atmosphere but these do not react to form oxides of nitrogen.

Statement II: The reaction between nitrogen and oxygen requires high temperature.

- (1) Both assertion and reason are correct, and the reason is the correct explanation for the assertion.
- (2) Both assertion and reason are correct, but the reason is not the correct explanation for the assertion.
- (3) The assertion is incorrect, but the reason is correct.
- (4) Both are assertion and reason are incorrect.

(JEE Main 2015)

4. The reaction of zinc with dilute and concentrated nitric acid, respectively produces:

- (1) NO<sub>2</sub> and N<sub>2</sub>O
- (2)  $N_2O$  and  $NO_2$
- (3) NO<sub>2</sub> and NO
- (4) NO and N<sub>2</sub>O

(JEE Main 2016)

- 5. The compound that does not produce nitrogen gas by the thermal decomposition is
  - $(1) (NH_4)_2 Cr_2 O_7$
- $(2) NH_4NO_2$
- $(3) (NH_4)_2 SO_4$
- (4)  $Ba(N_3)$ ,

(JEE Main 2018)

# JEE ADVANCED

# Single Correct Answer Type

- 1. The reaction of P with X leads selectively to P<sub>4</sub>O<sub>6</sub>. X is
  - (1) dry O<sub>2</sub>
  - (2) a mixture of O, and N,
  - (3) moist O<sub>2</sub>
  - (4) O<sub>2</sub> in the presence of aqueous NaOH (IIT-JEE 2009)
- 2. Extra pure N<sub>2</sub> can be obtained by heating
  - (1) NH<sub>3</sub> with CuO
- $(2) NH_4NO_3$
- $(3) (NH_4), Cr_5O_7$
- (4)  $Ba(N_3)_2$

(IIT-JEE 2011)

- 3. The reaction of white phosphorous with aqueous NaOH gives phosphine along with another phosphorous containing compound. The reaction type; the oxidation state of phosphorous in phosphine and in the other products are, respectively,
  - (1) redox reaction; -3 and -5
  - (2) redox reaction; +3 and +5
  - (3) disproportionation reaction; -3 and +5
  - (4) disproportionation reaction; -3 and +3

(IIT-JEE 2012)

- **4.** Which ordering of compounds is according to the decreasing order of the oxidation state of nitrogen?
  - (1) HNO<sub>3</sub>, NO, NH<sub>4</sub>Cl, N<sub>2</sub>
  - (2) HNO<sub>3</sub>, NO, N<sub>2</sub>, NH<sub>4</sub>Cl
  - (3) HNO<sub>3</sub>, NH<sub>4</sub>Cl, NO, N<sub>2</sub>

(4) NO, HNO<sub>3</sub>, NH<sub>4</sub>Cl, N<sub>2</sub>

(IIT-JEE 2012)

- 5. The product formed in the reaction of SOCl<sub>2</sub> (thionyl chloride) with white phosphorous is
  - (1) PCl<sub>3</sub>

(2)  $SO_2Cl_2$ 

(3) SCl<sub>2</sub>

(4) POCl<sub>3</sub>

(JEE Advanced 2014)

- 6. The order of the oxidation state of the phosphorus atom in H<sub>3</sub>PO<sub>2</sub>, H<sub>3</sub>PO<sub>4</sub>, H<sub>3</sub>PO<sub>3</sub> and H<sub>4</sub>P<sub>2</sub>O<sub>6</sub> is
  - (1)  $H_3PO_4 > H_4P_2O_6 > H_3PO_3 > H_3PO_2$
  - (2)  $H_3PO_3 > H_3PO_2 > H_3PO_4 > H_4P_2O_6$
  - (3)  $H_3PO_2 > H_3PO_3 > H_4P_2O_6 > H_3PO_4$
  - (4)  $H_3PO_4 > H_3PO_2 > H_3PO_3 > H_4P_2O_6$

(JEE Advanced 2017)

### **Multiple Correct Answers Type**

- 1. The nitrogen oxide(s) that contains N—N bond is/are
  - $(1) N_2O$

(2)  $N_2O_3$ 

 $(3) N_2O_4$ 

- (4) N<sub>2</sub>O<sub>5</sub> (IIT-JEE 2010)
- 2. The nitrogen containing compound produced in the reaction of HNO<sub>3</sub> with P<sub>4</sub>O<sub>10</sub>
  - (1) can also be prepared by reaction of P<sub>4</sub> and HNO<sub>3</sub>
  - (2) is diamagnetic
  - (3) contains one N-N bond
  - (4) react with Na metal producing a brown gas

### (JEE Advanced 2016)

- 3. The compound(s) which generate(s) N<sub>2</sub> gas upon thermal decomposition below 300°C is (are)
  - (1) NH<sub>4</sub>NO<sub>3</sub>
- (2)  $(NH_4)_2Cr_2O_7$
- (3)  $Ba(N_3)_2$
- (4) Mg<sub>3</sub>N<sub>2</sub>

(JEE Advanced 2018)

- **4.** Based on the compounds of group 15 elements, the correct statement(s) is (are)
  - (1) Bi<sub>2</sub>O<sub>5</sub> is more basic than N<sub>2</sub>O<sub>5</sub>
  - (2) NF<sub>3</sub> is more covalent than BiF<sub>3</sub>
  - (3) PH, boils at lower temperature than NH,
  - (4) N—N single bond is stronger than the P—P single bond

(JEE Advanced 2018)

#### **Linked Comprehension Type**

#### Paragraph 1

There are some deposits of nitrates and phosphates in the earth's crust. Nitrates are more soluble in water. Nitrates are difficult to reduce under laboratory conditions but microbes do it easily. Ammonia forms a large number of complexes with transition metal ions. Hybridisation easily explains the ease of sigma donation capability of NH<sub>3</sub> and PH<sub>3</sub>. Phosphine is a flammable gas and is prepared from white phosphorus.

- 1. Which of the following statements is correct?
  - (1) Phosphates have no biological significance in humans.
  - (2) Between nitrates and phosphates, phosphates are less abundant in earth's crust.
  - (3) Between nitrates and phosphates, nitrates are less abundant in earth's crust.
  - (4) Oxidation of nitrates is possible in soil.
- 2. Which of the following statements is correct?
  - (1) Between NH<sub>3</sub> and PH<sub>3</sub>, NH<sub>3</sub> is a better electron donor because the lone pair of electrons occupies spherical s-orbital and is less directional.
  - (2) Between NH<sub>3</sub> and PH<sub>3</sub>, PH<sub>3</sub> is a better electron donor because the lone pair of electrons occupies *sp*<sup>2</sup>-orbital and is more directional.

- (3) Between NH<sub>3</sub> and PH<sub>3</sub>, NH<sub>3</sub> is a better electron donor because the lone pair of electrons occupies *sp*<sup>3</sup>-orbital and is more directional.
- (4) Between NH<sub>3</sub> and PH<sub>3</sub>, PH<sub>3</sub> is a better electron donor because the lone pair of electrons occupies spherical *s*-orbital and is less directional.
- **3.** White phosphorus on reaction with NaOH gives PH<sub>3</sub> as one of the products. This is a
  - (1) dimerisation reaction
  - (2) disproportionation reaction
  - (3) condensation reaction
  - (4) precipitation reaction

(IIT-JEE 2008)

#### Paragraph 2

Upon heating  $KClO_3$  in the presence of catalytic amount of  $MnO_2$ , a gas W is formed. Excess amount of W reacts with white phosphorus to give X. The reaction of X with pure  $HNO_3$  gives Y and Z.

- 4. W and X are, respectively
  - (1) O<sub>3</sub> and P<sub>4</sub>O<sub>6</sub>
- (2)  $O_2$  and  $P_4O_{10}$
- (3)  $O_3$  and  $P_4O_{10}$
- (4)  $O_2$  and  $P_4O_6$
- 5. Y and Z are, respectively
  - (1)  $N_2O_4$  and  $H_3PO_3$
- (2) N<sub>2</sub>O<sub>4</sub> and HPO<sub>3</sub>
- (3) N<sub>2</sub>O<sub>5</sub> and HPO<sub>3</sub>
- (4) N<sub>2</sub>O<sub>3</sub> and H<sub>3</sub>PO<sub>4</sub>

(JEE Advanced 2017)

#### **Matrix Match Type**

1. Match each of the reactions given in Column I with the corresponding product(s) given in Column II.

	Column I		Column II
(a)	Cu + dil HNO <sub>3</sub>	p.	NO
(b)	Cu + conc HNO <sub>3</sub>	q.	NO <sub>2</sub>
(c)	Zn + dil HNO <sub>3</sub>	r.	N <sub>2</sub> O
(d)	Zn + conc HNO <sub>3</sub>	s.	Cu(NO <sub>3</sub> ) <sub>2</sub>
		t.	$Zn(NO_3)_2$

#### **Numerical Value Type**

1. What is the total number of diprotic acids among the following?

(IIT-JEE 2010)

2. Among the following, the number of compounds that can react with PCl<sub>5</sub> to give POCl<sub>3</sub> is

(IIT-JEE 2011)

3. The total number of compounds having at least one bridging oxo group among the molecules given below is\_\_\_\_\_.

$$N_{2}O_{3},\,N_{2}O_{5},\,P_{4}O_{6},\,P_{4}O_{7},\,H_{4}P_{2}O_{5},\,H_{5}P_{3}O_{10},\,H_{2}S_{2}O_{3},\,H_{2}S_{2}O_{5}$$

(JEE Advanced 2018)

# VERCISES

# Correct Answer Type

cingle Corre	ect Answer i	ype		
	<b>2.</b> (2)	<b>3.</b> (3)	<b>4.</b> (2)	<b>5.</b> (4)
1.(1)	7. (1)	<b>8.</b> (2)	9. (2)	<b>10.</b> (1)
6. (2)	<b>12.</b> (2)	<b>13.</b> (2)	<b>14.</b> (1)	<b>15.</b> (1)
11. (4)	<b>17.</b> (2)	<b>18.</b> (4)	<b>19.</b> (4)	<b>20.</b> (1)
16. (2) 21. (1)	<b>22.</b> (1)	<b>23.</b> (4)	<b>24.</b> (1)	<b>25.</b> (2)
<b>26.</b> (1)	<b>27.</b> (1)	<b>28.</b> (1)	<b>29.</b> (3)	<b>30.</b> (4)
31. (2)	<b>32.</b> (2)	<b>33.</b> (3)	<b>34.</b> (4)	<b>35.</b> (4)
<b>36.</b> (3)	<b>37.</b> (2)	<b>38.</b> (2)	<b>39.</b> (4)	<b>40.</b> (1)
<b>41.</b> (1)	<b>42.</b> (2)	<b>43.</b> (2)	<b>44.</b> (2)	<b>45.</b> (1)
46. (3)	<b>47.</b> (3)	<b>48.</b> (1)	<b>49.</b> (3)	<b>50.</b> (1)
51. (3)	<b>52.</b> (1)	<b>53.</b> (4)	<b>54.</b> (1)	<b>55.</b> (2)
56. (2)	<b>57.</b> (1)	<b>58.</b> (3)	<b>59.</b> (2)	<b>60.</b> (3)
61. (4)	<b>62.</b> (3)	<b>63.</b> (3)	<b>64.</b> (4)	<b>65.</b> (2)
<b>66.</b> (3)	<b>67.</b> (3)	<b>68.</b> (3)	<b>69.</b> (4)	<b>70.</b> (3)
71.(3)	<b>72.</b> (3)	<b>73.</b> (3)	<b>74.</b> (3)	<b>75.</b> (2)
<b>76.</b> (1)	<b>77.</b> (1)	<b>78.</b> (4)	<b>79.</b> (1)	<b>80.</b> (1)
<b>81.</b> (3)	<b>82.</b> (3)	<b>83.</b> (1)	<b>84.</b> (1)	<b>85.</b> (4)
<b>86.</b> (1)	<b>87.</b> (2)	<b>88.</b> (2)	<b>89.</b> (1)	<b>90.</b> (1)
<b>91.</b> (3)	<b>92.</b> (2)	<b>93.</b> (4)	<b>94.</b> (4)	<b>95.</b> (3)
<b>96.</b> (1)	<b>97.</b> (1)	<b>98.</b> (1)	<b>99.</b> (1)	<b>100.</b> (4)
<b>101.</b> (1)	<b>102.</b> (1)	<b>103.</b> (2)	<b>104.</b> (4)	<b>105.</b> (1)
<b>106.</b> (1)	<b>107.</b> (2)	<b>108.</b> (2)	<b>109.</b> (2)	<b>110.</b> (1)
111. (2)	<b>112.</b> (4)	<b>113.</b> (1)	<b>114.</b> (4)	<b>115.</b> (1)
<b>116.</b> (3)	<b>117.</b> (3)		Ç.	

#### **Multiple Correct Answers Type**

Multiple coll		.,,,,		
<b>1.</b> (1, 2, 4)	<b>2.</b> (1, 2, 4)	<b>3.</b> (1, 2, 4)	<b>4.</b> (1, 2)	<b>5.</b> (1, 4)
<b>6.</b> (2, 4)	<b>7.</b> (3, 4)	<b>8.</b> (1, 2)	<b>9.</b> (1, 2, 3)	<b>10.</b> (3, 4)
11. (2, 3, 4)	<b>12.</b> (1, 2, 3, 4)	<b>13.</b> (1, 2, 3)	<b>14.</b> (1, 3, 4)	<b>15.</b> (1, 3)
<b>16.</b> (1, 2, 3, 4)	<b>17.</b> (1, 2, 4)	<b>18.</b> (2, 3)	<b>19.</b> (1, 2, 3)	<b>20.</b> (1, 2)
<b>21.</b> (1, 2, 3)	<b>22.</b> (1, 2, 3)	<b>23.</b> (1, 3)	<b>24.</b> (2, 3)	<b>25.</b> (3, 4)
<b>26.</b> (3, 4)	<b>27.</b> (2, 3, 4)	<b>28.</b> (2, 3)	<b>29.</b> (1, 2)	<b>30.</b> (2, 3)
<b>31.</b> (2, 3)	<b>32.</b> (2, 4)	<b>33.</b> (1, 3)	<b>34.</b> (4)	<b>35.</b> (1, 2, 4)
<b>36.</b> (1, 3, 4)	<b>37.</b> (1, 2)	<b>38.</b> (1, 2, 3)		

#### **Linked Comprehension Type**

1. (2)	<b>2.</b> (3)	<b>3.</b> (3)	<b>4.</b> (3)	<b>5.</b> (2)
6. (4)	7. (1)	<b>8.</b> (3)	<b>9.</b> (2)	<b>10.</b> (3)
11. (4)	<b>12.</b> (1)	<b>13.</b> (1)	<b>14.</b> (2)	<b>15.</b> (3)
16. (2)	17. (3)	<b>18.</b> (1)	<b>19.</b> (2)	<b>20.</b> (3)
21 (3)	22 (4)			

#### **Matrix Match Type**

Q. No.	(a)	(b)	(c)	(d)
1.	S .	p	q	r

2.	r	s	q	p
3.	r	р	q	S
4.	p	r	S	q
5.	. r	q	р	S
6.	q	р	S	r
7.	S	r	q	р
8.	r	q	S	р
9.	q	r	S	р
10.	S	р	q	г
11.	iii–p	iv–q	i–s	ii–r
12.	i, ii–q,s	iv-r,	v-t,	iii–p

### 13. (c) 14. (b) 15. (d) 16. (a)

#### **Numerical Value Type**

1. (5)	<b>2.</b> (2)	<b>3.</b> (3)	<b>4.</b> (6)	<b>5.</b> (4)
<b>6.</b> (4)	7. (4)	<b>8.</b> (6)	<b>9.</b> (4)	<b>10.</b> (6)
11. (4)	<b>12.</b> (1)	<b>13.</b> (5)	<b>14.</b> (4)	<b>15.</b> (2)
<b>16.</b> (4)	17. (6)	<b>18.</b> (2)	<b>19.</b> (2)	<b>20.</b> (8)
<b>21.</b> (3.2)	<b>22.</b> (2.5)			

#### **ARCHIVES**

#### JEE Main

#### **Single Correct Answer Type**

<b>1.</b> (1) <b>2.</b> (1)	<b>3.</b> (1)	<b>4.</b> (2)	<b>5.</b> (3)
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#### JEE Advanced

#### **Single Correct Answer Type**

1. (2)	<b>2.</b> (4)	<b>3.</b> (3)	<b>4.</b> (2)	<b>5.</b> (1)
<b>6.</b> (1)				

#### **Multiple Correct Answers Type**

1. (1: 2: 3)	2 (2 4)	3 (2 3)	4 (1 2 3)

#### **Linked Comprehension Type**

1. (	(3)	) 2. (	3	<b>3.</b> (2	)	4. (	2	) 5.	0	2)	۱
1. (	)	, 4. (	,	) 3. (~	- )		_	,	1.	-,	

#### **Matrix Match Type**

#### **Numerical Value Type**

# p-Block **Group 16 Elements** The Oxygen Family

# **OVERVIEW**

- 1. Group 16 elements are known as chalcogens, i.e. ore forming elements.
- 2. General electronic configuration:  $ns^2np^4$
- 3. Oxygen is the most abundant element. Sulphur is the 16th most abundant element. The last member Po is radioactive.
- 4. Oxygen is a gas, while rest of the members are solids.
- 5. Oxygen is diatomic, while other exists as S<sub>8</sub>, Se<sub>8</sub>, Te<sub>8</sub>.
- 6. Atomic radii: O < S < Se < Te < Po
- 7. Ionisation enthalpy: O > S > Se > Te > Po
- 8. Electronegativity: O > S > Se > Te > Po
- 9. Electron gain enthalpy: O < S > Se < Te < Po
- 10. Metallic character: Increases with increase in atomic number.

- 11. Allotropy: All the members show allotropy
  - Oxygen: O<sub>2</sub> and O<sub>3</sub>
  - Rhombic, monoclinic, plastic and amorphous Sulphur:

Selenium: Red and grey form

- 12. Oxidation state: Oxygen because of high electronegativity shows an oxidation state of -2.
- 13. Catenation: O < S > Se > Te > Po

Catenating ability depends on E-E bond strength (where E = O, S, Se, Te and Po)

14. Oxidation states:

Tendency to show -2 oxidation state decreases down the group. The compounds having +4 oxidation state show both oxidising and reducing properties while compounds having +6 oxidation states are only oxidising.

- 15. All elements form hydroxides of the type of H<sub>2</sub>E, where E = O, S, Se, Te and Po.
  - i. Covalent character:  $H_2O < H_2S < H_2Se < H_2Te$
  - ii. Thermal stability:  $H_2O > H_2S > H_2Se > H_2Te$
  - iii. Acidic nature:  $H_2O < H_2S < H_2Se < H_2Te$
  - iv. Reducing agent:  $\rm H_2O < \rm H_2S < \dot{\rm H}_2Se < \rm H_2Te$ v. Volatility:  $H_2O >> H_2S > H_2Se > H_2Te$

- vi. Boiling point:  $H_2O(373 \text{ K}) > H_2\text{Te}(269 \text{ K}) >$  $H_2$ Se (232 K) >  $H_2$ S (213 K)
- vii. Melting point:  $H_2O(273 \text{ K}) > H_2Te(222 \text{ K}) >$  $H_2$ Se (208 K) >  $H_2$ S (188 K)
- viii. Melting point:  $H_2O$  (273 K) >  $NH_3(195.2 \text{ K}) > HF$ (190 K)
- ix. Boiling point:  $H_2O$  (373 K) > HF (293 K) >  $NH_3$ (238.5 K)
- 16. S, Se Te and Po form oxides on burning in air of the type MO<sub>2</sub>, e.g., SO<sub>2</sub>, SeO<sub>2</sub>, TeO<sub>2</sub> and PoO<sub>2</sub>.
  - i. Acidic strength:  $SO_2 > SeO_2 > TeO_2 > PoO_3$
  - ii. Stability:  $SO_2 > SeO_2 > TeO_2 > PoO_3$
  - S, Se and Te also form trioxides. The trioxides are acidic in nature. Acidic nature  $SO_3 > SeO_3 > TeO_3$
- 17. Sulphur, selenium and tellurium form similar oxyacids.

		corm similar oxyacius.	
$H_2SO_3$	$H_2SeO_3$	H,TeO,	_
Sulphurous acid Salts: Sulphites	Selenous acid	Tellurous acid	nercases
Saits: Suipnites	Selenites		
H <sub>2</sub> SO <sub>4</sub> Sulphuric acid Salts: Sulphates	H <sub>2</sub> SeO <sub>4</sub> Selenic acid Selenates	H <sub>2</sub> TeO <sub>4</sub> Telluric acid Tellurates	Strength

Strength increases

18. S, Se and Te form hexafluorides of type  $MF_6$ .  $SF_6$  is extremely inert. SeF<sub>6</sub> is slightly reactive while TeF<sub>6</sub> is hydrolysed by water into H6TeO6. Many tetrahalides are known. SF<sub>4</sub> is a gas, SeF<sub>4</sub> is a liquid while TeF<sub>4</sub> is a solid. S, Se, Te and Po form tetrachlorides and bromides while Te and Po form tetraiodides

All elements except Se form stable dichlorides and dibromides.

Dimeric monohalides as S<sub>2</sub>F<sub>2</sub>, S<sub>2</sub>Cl<sub>2</sub> and S<sub>2</sub>Br<sub>2</sub> are known.

19. Only S and Se form oxyhalides. They are called thionyl and selenyl halides.

 $\mathrm{SOF}_2 \quad \mathrm{SOCl}_2 \quad \mathrm{SOBr}_2 \quad \mathrm{SeOF}_2 \quad \mathrm{SeOCl}_2 \quad \mathrm{SeOBr}_2$ They react with water readily.

- 20. It occurs in the atmosphere to the extent of 21% by volume and 23% by mass.
- 21. Oxygen combines nearly with all the elements except inert gases, noble metals and halogens. The binary compounds of

oxygen with other elements are called oxides. However, the compounds of oxygen and fluorine are termed as fluorides, as fluorine is more electronegative than oxygen.

- **22.**  $O_3$  is an allotrope of  $O_2$ .
- 23.  $O_3$  acts as a powerful oxidising agent.  $(O_3 \longrightarrow O_2 + O)$  is a good bleaching agent. It bleaches oil, ivory, flour, starch waxes, pulp etc.
- 24. Mercury is oxidised by ozone to suboxide ( $Hg_2O$ ) which dissolves in mercury. It starts sticking to glass and loses mobility. The mercury loses its meniscus. This is termed as the tailing of mercury.
- 25. Sulphur forms a number of oxides such as  $S_2O$ , SO,  $S_2O_3$ ,  $SO_2$ ,  $SO_3$ ,  $S_2O_7$  and  $SO_4$ . Out of these,  $SO_2^-$  and  $SO_3$  are important and common.

These act as reducing as well as oxidising agents. In presence of moisture, these act as bleaching agents. The bleaching action is due to reduction. The bleaching is temporary.

- 26. A large number of oxyacids are known in the case of sulphur either in free state or in the form of salts or both. Oxyacids with S-S links are called thioacids. Acids having sulphur in lower oxidation state belong to -ous series while those having sulphur in higher oxidation state belong to -ic series.
- 27. Sulphuric acid (H<sub>2</sub>SO<sub>4</sub>): It is considered as king of chemicals. In ancient days, it was called an oil of vitriol as it was obtained by distilling ferrous sulphate (green vitriol).
- 28. Contact process: The process involves the conversion of  $SO_2$  into  $SO_3$  by air in presence of a catalyst (platinum or  $V_2\bar{O}_5$ ). Best results are obtained when  $SO_2$  and  $O_2$  are present in molecular proportion of 2:3. The optimum temperature is 450°C.
- 29. H<sub>2</sub>SO<sub>4</sub> is a strong dibasic acid and forms two series of salts: (i) bisulphites and (ii) sulphates.
- 30. Thiosulphuric acid (H<sub>2</sub>S<sub>2</sub>O<sub>3</sub>): It is a dibasic acid. It does not exist in free state. Salts are quite stable. Thiosulphates are reducing agents.
- 31. Permonooxy sulphuric acid or Caro's acid (H,SO5): It is a diabasic, stable and crystalline solid. It has a peroxolinkage

$$\begin{pmatrix} O \\ O \end{pmatrix} S - O - O - H \end{pmatrix}$$

It is a strong oxidising agent.

32. Peroxydisulphuric acid or Marshall's acid (H<sub>2</sub>S<sub>2</sub>O<sub>8</sub>): |tis a strong and the strong acid of the stron Peroxyulsurphia a peroxolinkage. It is a strong oxidising agent.

33. Dithionic acid (H<sub>2</sub>S<sub>2</sub>O<sub>6</sub>): It is a dibasic acid. It does how exist in free state but its salts are quite stable.

Two S atom are in different oxidation state of +5 and +3

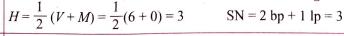
### 34. Uses:

- a.  $SF_6$  is used in high voltage transformers because of its insulating property.
- b. Liquid oxygen mixed with finely divided carbon is used in place of dynamite in coal mining.
- c. A mixture of ozone and cyanogen is used as a rocket
- d. Gun powder is a mixture of sulphur, charcoal and KNO.
- e.  $S_2Cl_2$  is used in the vulcanisation of rubber. It is heating rubber with sulphur and was discovered by Charles Goodyear in 1839.
- f. Electrical conductivity of Se is negligible in dark but increases on exposure to light. Due to this property, & is used in photo-electric cells and as a photoconductor in photocopying (Xerox) machines. It is also used as decolouriser of glass.
- Tellurium is used as an additive in metallurgy for the manufacture of iron, steel, non-ferrous metals and alloys.
- 35. The chemical reactions of ozone with oxides of nitrogen and with chlorofluoro-alkanes are responsible for the depletion of ozone shield of the atmosphere. This is called 'ozone hole'. It is feared that this will allow, an excessive amount of UV light to reach the earth which will cause melanoma (skin cancer) in humans.

**36.** Some examples of hybridisation of group 16 ( $6e^{\Theta}$ ):

SO<sub>2</sub> (Sulphur Dioxide) O=S=O

[one  $(p\pi-p\pi)$  and one  $(p\pi-d\pi)$  multiple bond]



 $\mu \neq 0$ 

 $H = sp^2$ ,

 $1(p\pi - p\pi)$  multiple bond

 $1(p\pi - d\pi)$  multiple bond

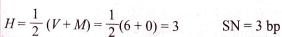
G = Planar, Shape = V or Bent

 $1(p\pi - p\pi)$  multiple bond  $2(p\pi - d\pi)$  multiple bond

SO<sub>2</sub> (Sulphur trioxide)

2.

[one  $(p\pi-p\pi)$  and two  $(p\pi-d\pi)$  multiple bond]  $O(\pi-d\pi)$ 



 $H = sp^2$ 

G = Planar

3.	н-Ё-н
	$(H_2S)$

 $\mu \neq 0$ 

 $\mu \neq 0$ 

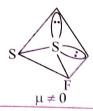
$$SN = 2 bp + 2 lp = 4$$
,  $H = sp^3$ ,  $G = T.H.$  (Shape) = V-shaped

4.

$$SF_2$$
  
 $(F-S-F)$ 

 $\mu \neq 0$ 

$$\mu \neq 0$$



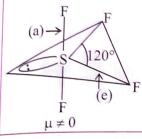
$$SN = 2 bp + 2 1p = 4$$
,  $H = sp^3$ ,  $G = T.H.$  (Shape) = V or Bent

$$SF_4 \left( \begin{matrix} F \\ F \end{matrix} \right) S \left( \begin{matrix} F \\ F \end{matrix} \right)$$

$$\operatorname{SeF}_{4}\left( \begin{array}{c} F \\ F \end{array} \right) = \left( \begin{array}{c} F \\ F \end{array} \right),$$

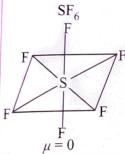
$$\operatorname{SeF}_{4}\left(\begin{array}{c} F \\ \end{array}\right)$$
,  $\operatorname{TeCl}_{4}\left(\begin{array}{c} Cl \\ Cl \end{array}\right)$   $\operatorname{TeCl}_{4}\left(\begin{array}{c} Cl \\ Cl \end{array}\right)$ 

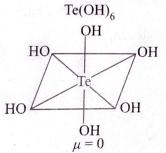
$$SN = 4 \text{ bp} + 1 \text{ lp} = 5$$
,  $H = sp^3$ ,  $G = Trigonal bipyramid$ ,  $Shape = See-saw or (distorted tetrahedral)$ 



Note: In T.b.p. geometry, lone pair will be on equatorial position (e) due to less repulsion (angle 120°) and hence stable.

6.

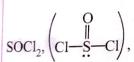




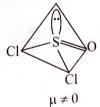
SN = 6 bp,

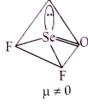
$$H = sp^3d^2,$$

Geometry = O.H.



-Cl), SeOF<sub>2</sub>,  $\begin{pmatrix} O \\ \parallel \\ F - Se - F \end{pmatrix}$ , [one  $(p\pi - p\pi)$  multiple bond]





SN = 3 bp + 1 lp = 4,

$$H=sp^3,$$

$$G = T.H.$$

$$H = sp^3$$

$$G = 1.H.$$

Note: Oxoacids and peroxoacids and their ions have same hybridisation, geometry and shape.

 $H_2SO_3$ , (Diabasic, O.S. = +4)

$$SO_3^{2-}$$

[one  $(p\pi-p\pi)$  multiple bonds]

Sulphurous acid,

Bisulphite ion or

Sulphite ion

Hydrogen sulphite ion

$$\begin{array}{ccc}
O & O & O \\
S & O & | & & \\
S & O & | & & \\
\mu \neq 0 & & & \\
Due to three equivalent resonance structure
\end{array}$$

SN = 3 bp + 1 lp = 4,

$$H=sp^3,$$

$$G = T.H.$$
 Shape = Pyramidal

15.

1. St

2. St (i)

(iii

3. S

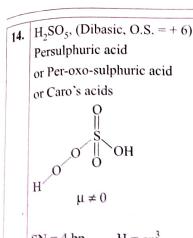
(i)

(ii

13. HS<sub>2</sub>O<sub>6</sub><sup>⊖</sup>  $S_2O_6^{2-}$ Dithionic acid (H<sub>2</sub>S<sub>2</sub>O<sub>6</sub>) [4(p $\pi$ -d $\pi$ ) multiple bond] Dithionate ion (Dibasic, O.S. = +5) Hydrogen dithionate ion  $H_2S_2O_6$ 

 $SN = 4 \text{ bp}, \qquad H = sp^3, \qquad Geometry = T.H.$ Due to three equivalent resonance structure

[2 (p $\pi$ -d $\pi$ ) multiple bonds]



HSO<sub>5</sub><sup>⊖</sup> Hydrogen per oxosulphate ion

 $SO_5^{2-}$ Peroxo-sulphate ion

$$SN = 4 \text{ bp}, \qquad H = sp^3,$$

Geometry = T.H.

15. Peroxydisulphuric acid or Perdisulphuric acid or Marshall's acid  $(H_2S_2O_8)$ . (Dibasic, O.S. = +6)

Oxyacids of sulphur are listed in five groups:

- 1. Sulphoxylic acid (H<sub>2</sub>SO<sub>2</sub>)
- 2. Sulphurous acid series:

(i) Sulphurous acid  $(H_2SO_3)$  (ii) Hyposulphurous or Dithionous acid (H<sub>2</sub>S<sub>2</sub>O<sub>4</sub>)

OH 
$$S_2^{+3}$$
  $S_2^{+3}$   $S_2^{+3}$   $S_2^{+3}$   $S_2^{+3}$   $S_2^{+3}$ 

(iii) Thiosulphurous acid  $(H_2S_2O_2)$ 



(iv) Di or Pyrosulphurous acid  $(H_2S_2O_5)$ 

- 3. Sulphuric acid series:
- (i) Sulphuric acid (H<sub>2</sub>SO<sub>4</sub>)
  - (ii) Thiosulphuric acid (H<sub>2</sub>S<sub>2</sub>O<sub>3</sub>)

$$HO \underset{\square}{\overset{O}{\underset{\parallel}{\longrightarrow}}} OH$$

$$\begin{array}{c}
S^0 \\
\parallel \\
S^{+4}
\end{array}$$
HO OH

(iii) Pyrosulphuric acid (H<sub>2</sub>S<sub>2</sub>O<sub>7</sub>)

- 4. Thionic acid series:
  - (i) Dithionic acid  $(H_2S_2O_6)$ O O S+5

(ii) Polythionic acid (H<sub>2</sub>S<sub>n</sub>O<sub>6</sub>)

$$\begin{array}{c} O \\ \parallel \\ S - (S) \xrightarrow[n-2]{} \begin{array}{c} O \\ \parallel \\ S \\ O \end{array} \\ O H \end{array}$$

For Example:

(a) Trithionic acid (when n = 3) ( $H_2S_3O_6$ )

$$\begin{array}{c} O & O \\ S - S - S \\ 0 & S \\ 0 & O \end{array} O H$$

(b) Tetrathionic acid (when n = 4) (H<sub>2</sub>S<sub>4</sub>O<sub>6</sub>)

(c) Pentathionic acid (when n = 5) ( $H_2S_5O_6$ ) and so on.

- 5. Peroxo acid series:
  - (i) Permonooxo sulphuric acid or Caro's acid (H<sub>2</sub>SO<sub>5</sub>)

(ii) Peroxodisulphuric acid or Marshall's acid (H<sub>2</sub>S<sub>2</sub>O<sub>8</sub>).

$$\begin{array}{c} O & O \\ S & O \\ O & O \\ O & O \end{array}$$

# INTRODUCTION

Group 16 elements are known as group of chalcogens. The name is derived from the Greek word for brass and points to the association of sulphur (S) and its congeners with copper (Cu). Most Cu minerals contain either oxygen or sulphur and frequently the other members of the group.

# 3.2 ABUNDANCE AND OCCURRENCE

Oxygen is the most abundant of all the elements. It occurs in the free form as dioxygen molecule (O<sub>2</sub>) and makes up 20.46% by volume and 23% by mas of the atmosphere. It also occurs in the form of ozone (O<sub>3</sub>), an allotrope of oxygen, in the upper atmosphere which protects us from the harmful radiations of the

Oxygen makes up 46.6% by weight of the earth's crust where it mainly occurs as silicate minerals. Oxygen also occurs in many metal oxide ores and as deposits of oxosalts such as carbonates, sulphates, nitrates and borates. It also makes up 89% by weight of water in oceans.

Sulphur, on the other hand, occurs less abundantly. Sulphur is the 16th most abundant element and constitutes 0.03 to 0.1% by mass of earth's crust. It occurs mainly, in the combined state, as sulphates such as gypsum, CaSO<sub>4</sub>·2H<sub>2</sub>O; epsom salt MgSO<sub>4</sub>·7H<sub>2</sub>O; baryte, BaSO<sub>4</sub> and as sulphides such as galena PbS; zinc blende, ZnS and copper pyrites, CuFeS<sub>2</sub>. Trace<sub>1</sub> of sulphur occur as hydrogen sulphide in volcanoes. Organic materials such as eggs, proteins, garlic, onion, hair, mustard and wool also contain sulphur.

Selenium and tellurium are less abundant than sulphur and occur as sellenides and tellurides in sulphide ores. Polonium is even less abundant in the earth crust, where it occurs as deca product in thorium and uranium minerals.

# 3.3 ATOMIC AND PHYSICAL **PROPERTIES**

The important atomic and physical properties of group 16 alono with electronic configuration are given in Table 3.1 and are discussed in the following sections.

Table 3.1 Atomic and physical properties of group 16 elements

Property		Element								
	Oxygen	Sulphur	Selenium	Tellurium	Polonium					
Symbol	О	S	Se	Те	Po					
Atomic number	8	16	34	52	84					
Atomic mass / (g mol <sup>-1</sup> )	16.00	32.06	78.96	127.60	210.00					
Electronic configuration	[He] $2s^22p^4$	[Ne] $3s^23p^4$	[Ar] $3d^{10}4s^24p^4$	[Kr] $4d^{10}5s^25p^4$	[Xe] $4f^{14} 5d^{10} 6s^2 6p^4$					
Covalent radius / (pm) <sup>a</sup>	66	104	117	137	146					
Ionic radius / (pm)	140	184	198	221	230 b					
Ionisation enthalpy, $\Delta_i H_1$	1314.0	1000	941	869	813					
$\Delta_i H_2 (\Delta_i H) / (kJ \text{ mol}^{-1})$	3388	2251	2045	1790	_					
Electronegativity	3.50	2.44	2.48	2.01	1.76					
Electron gain enthalpy $\Delta_{ep} H^{\Theta}$ / (kJ mol <sup>-1</sup> )	-141	-200	÷195	-190	-174					
Density (g cm <sup>3</sup> -) / 298 K	1.32 <sup>c</sup>	$2.06^d$	4.19 <sup>c</sup>	6.25						
Melting point / (K)	55	393 <sup>f</sup>	490	725	520					
Soiling point / (K)	90	718	958	1260	1235					
exidation states*	-2, -1, -1, +1, +2	-2, +2, +4, +6	-2, +2, +4, +6	-2, +2, +4, +6	+2, +4					

<sup>b</sup> Approximate value, <sup>c</sup> At the melting point, <sup>d</sup> Rhombic sulphur, <sup>e</sup> Hexagonal grey, Note: a Single bond, <sup>f</sup> Monoclinic form at 673 K. Oxygen shows oxidation states of +2 and +1 in oxygen fluorides OF<sub>2</sub> and O<sub>2</sub>F<sub>2</sub> respectively.

## 3.3.1 ELECTRONIC CONFIGURATION

General valence shell electronic configuration of 16 elements is  $ns^2np^4$ , i.e. they have six electrons in the valency shell. Since the differentiating electron enters in the p-orbital, group 16 elements are also p-block elements. Electronic configuration of group 16 elements is given in Table 3.1.

# 3.3.2 Atomic and Ionic Radii

The atomic radii of group 16 elements are smaller than those of the corresponding group 15 elements. This is due to increase in effective nuclear charge on moving from group 15 to group 16. which results in greater attraction of the electrons by nucleus

Consequently atomic radii decreases, e.g. atomic radii of N is more than atomic radii of O.

Down the group  $(\downarrow)$ , i.e., from O to Po, atomic radii as well as ionic radii (Table 3.1) increase. This increase is primarily due to increase in number of electron shells down the group.

# 3,3.3 IONISATION ENTHALPY (IE) OR $(\Delta_i H^{\odot})$

pown the group  $(\downarrow)$ , i.e. from O to Po, ionisation enthalpy decreases. This is due to increasing atomic radii and hence increasing shielding effect of the inner electrons or decreasing effective nuclear charge down the group.

$$(IE_1 \text{ or } \Delta_i H_1^{\odot}): O > S > Se > Te > Po$$

The first ionisation enthalpies  $(\Delta_1 H_1)$  of the group 16 elements are unexpectedly lower while their second ionisation enthalpies (AH<sub>2</sub>) are higher than those of the corresponding group 15 elements.

The first ionisation enthalpy  $(\Delta_i H_1)$  of group 16 elements is lower than those of group 15 elements despite their smaller atomic radii and higher nuclear charge. This is due to the relatively symmetrical and more stable electronic configuration of group 15 elements as compared to those of group 16 elements.

### 3.3.4 ELECTRONEGATIVITY (EN)

The electronegativity values of group 16 elements are higher than the corresponding group 15 elements. This is due to smaller atomic radii or group 16 elements as compared to group 15 elements. Oxygen is the second most electronegative element (EN = 3.5), the first being fluorine (EN = 4.0).

Down the group  $(\downarrow)$ , electronegativity decreases.

The electronegativity of sulphur is, however, much lower than that of oxygen. This is probably due to an unexpected increase in the size of sulphur (107 pm) as compared to that of oxygen (66 pm). Thereafter, the electronegativity decreases slowly but regularly from selenium to polonium as the size of atom increases slowly but regularly.

Further since after oxygen there is a steep drop in electronegativity of S, Se, Te and Po, therefore, their compounds have less ionic character as compared to those of oxygen.

# 3.3.5 ELECTRON GAIN ENTHALPY $(\Delta_{eg} H^{\odot})$

The elements of group 16 have two electrons less than the nearest noble gas configuration. Therefore, they have a high tendency to accept two additional electrons and hence have large negative electron gain enthalpies next only to the halogens. The electron gain enthalpy of oxygen is, however, least negative in this group. This is due to its small size. As a result of which, the electron repulsions in the relatively small 2p-subshell are comparatively large and hence the incoming electrons are not accepted with the same ease as in case of other elements of this group.

# 3.3.6 Non-Metallic and Metallic Character

Elements of group 16 are less metallic due to high ionisation enthalpy values. Down the group (\$\psi\$), with the decrease in ionisation enthalpy values, metallic character increases. Thus oxygen and sulphur are typical non-metals. Sulphur acts as an insulator; selenium and tellurium though essentially non-metallic, show some metallic character as well and hence may be called as metalloids. Thus Se and Te behave as semiconductors. The last

member of this group, i.e. polonium is however metallic in nature but is radioactive with a short half life (13.8 days).

#### 3.3.7 MELTING AND BOILING POINTS

Down the group  $(\downarrow)$ , melting and boiling points increase regularly from oxygen to tellurium. However, melting and boiling points of polonium are lower than those of tellurium.

This is due to the fact that down the group  $(\downarrow)$ , with the increase in atomic size or atomic mass, van der Waals forces of attraction also increase and hence melting and boiling points increase regularly from oxygen to tellurium. However, at polonium due to maximum number of intervening d- and f-electrons, the inert pair effect exists in Po. Consequently, the ns and np valence electrons in Po are less available and hence van der Waals forces of attraction will be weaker in Po as compared to Te. Hence melting and boiling points of Po will be less than that

#### 3.3.8 ELEMENTAL STATE

Oxygen exists as a diatomic gas at room temperature while other elements (S, Se and Te) exist as octa-atomic solids. Due to small size and high electronegativity, oxygen atom forms  $p\pi$ – $p\pi$  double bond with other oxygen atom to form O = O molecule. The intermolecular forces of attraction between oxygen molecules are weak van der Waals forces and hence oxygen exists as a diatomic gas at room temperature.

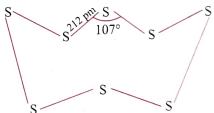


Fig. 3.1 Puckered 8-membered ring structure of sulphur molecule  $(S_8)$ 

However, the rest of elements of this group do not form  $p\pi$ – $p\pi$ multiple bonds due to their larger size and hence do not exist as diatomic (M2) molecules. Instead they prefer to form single bonds and have complex structures. For example, S, Se and Te exist as octa-atomic molecules (S<sub>8</sub>, Se<sub>8</sub> and Te<sub>8</sub>) having puckered 8-membered crown shaped rings (Figure 3.1).

## 3.3.9 MULTIPLE BONDING

Oxygen forms  $p\pi$ – $p\pi$  double bonds but other elements do not. However, S and other elements of this group possess d-orbitals and hence form  $p\pi - d\pi$  multiple bonds. To obtain effective  $p\pi - d\pi$ overlap, the size of d-orbital must be similar to that of p-orbital. Thus, sulphur forms stronger  $p\pi$ - $d\pi$  bonds than the larger elements of this group. Down the group, i.e. from S to Se, tendency to form  $p\pi$ – $p\pi$  multiple bond decreases.

## 3.3.10 CATENATION

The tendency of atoms of the same element to link together to form chains and rings is known as catenation. Amongst group 16 elements, oxygen has lesser catenating ability as compared to sulphur. Further from S to Po, catenating ability decreases. The catenation phenomenon is dependent on E-E bond strength.

Because of stronger S—S bonds as compared to O—O bonds, sulphur has a stronger tendency for catenation than oxygen. This can be explained as follow.

Due to small size, the lone pairs of electrons on the oxygen atoms repel the bond pair of the O—O bond to a greater extent than the lone pairs of electrons on the sulphur atoms in S—S bond. As a result, S—S bond is much stronger (213 kJ mol<sup>-1</sup>) than O—O bond (138 kJ mol<sup>-1</sup>) and hence sulphur has a much stronger tendency for catenation than oxygen. Further, as the size of the atom increases down the group from S to Po, the strength of the element—element bond decreases and hence the tendency for catenation decreases accordingly.

#### 3.3.11 ALLOTROPY

The phenomenon by which an element exists in two or more different crystalline or amorphous forms is called allotropy and the different forms are called allotropic forms or allotropes of the given element. Different allotropic forms of an element have different physical properties but similar chemical properties.

**Allotropes of oxygen:**  $O_2$  (dioxygen) and  $O_3$  (Ozone). (For more details refer to Sections 3.7 and 3.8)

**Allotropes of sulphur:** Rhombic, monoclinic, plastic and amorphous. (For more details refer to Section 3.10)

Allotropes of selenium: Six allotropes are known. There are three red non-metallic forms containing Se<sub>8</sub> rings. They differ in the way the rings are packed in the crystal. An amorphous red form contains polymeric chains. There are in addition two grey forms. The most stable is the grey metallic forms, which contains infinite spiral chains of Se atoms with weak metallic interaction between adjacent chains. Grey selenium is the only allotrope of selenium which conducts electricity.

**Allotropes of tellurium:** Tellurium has only one crystalline form, which is silvery white and semi-metallic. It is similar to grey Se, but has stronger metallic interaction.

Allotropes of polonium: Polonium is a true metal. It exists as an  $\alpha$ -form which is cubic and a  $\beta$ -form which is rhombohedral. Both forms are metallic. Thus, there is a marked decrease in the number of allotropic forms from S to Se to Te.

Note: Photosensitive elements: The grey form of selenium (metallic) and tellurium consists of parallel chains held by weak metallic bonds. In the presence of light, the weak metallic bonds are excited and as a result, the number of free electrons increases and so does the conductivity. Thus, these elements conduct electricity significantly only in presence of light. That is why Se and Te are called photosensitive elements. Further since conduction increases with intensity of light, selenium is particularly used for measuring the intensity of light

# 3.4 OXIDATION STATES

O.S. is defined as the residual charge left on the atom where other atoms are removed as ions. Since all the elements of this group have  $ns^2np^4$  configuration in their valence shell (outermost orbit), they can attain noble gas configuration viz.  $ns^2np^6$  either by gaining or by sharing electrons. These elements, therefore, show two types of oxidation state.

1. Negative oxidation state: The high electronegativity of oxygen indicates that it will tend to complete its octet preferably by gaining electron. Because of this, almost all

metal oxides are ionic and contain  $O^{2-}$  ions in which  $oxyge_{\theta}$  exhibits an oxidation state of -2.

Even if the octet is completed by sharing of electrons,  $th_{ese}$  electrons, for the purpose of determining the oxidation stale, are counted towards oxygen because, except  $OF_2$ ,  $oxyge_n$  forms the more electronegative atom in all its compounds. Oxygen thus exhibits an oxidation state of -2.

In addition, oxygen shows an oxidation state of (i)  $\sim 1_{1/1}$  peroxides such as  $H_2O_2$ , (ii) -1/2 in superoxides such as  $KO_2$  and (iii) +1 in  $O_2F_2$  and +2 in  $OF_2$ .

The electronegativity of these elements are, however, low Their compounds, even with most electropositive elements, are rarely more than 50% ionic.

Since the electronegativities decrease down the group i.e. O to Po, the tendency of elements to show -2 oxidation state decreases down the group from sulphur to polonium. Hence there is much less probability of the formation of the dinegative ions in case of S, Se and Te. The least electronegative element, polonium, in fact does not exhibit negative oxidation state at all. Rather it shows +2 oxidation state.

2. Positive oxidation states: Since electronegativity of oxygen is very high, it exhibits only a negative oxidation state. It shows no positive oxidation state, except in O<sub>2</sub>F<sub>2</sub> and OF<sub>2</sub>. In the case of other elements, since electronegativities decrease (and also the ionisation energies decrease) down the group towards heavier elements, positive oxidation states become more frequent. The electronic configuration  $ns^2np^4$  for the outer shell suggests that these elements can have three positive oxidation states, viz, +2, +4 and +6. The +2 and +4 states are shown when only the *p*-electrons are involved, as explained below.

mvorved, as explained below.					
2s $2p$					
O atom in the ground state 1 1 1 1 1					
There are no <i>d</i> -orbitals Excitation not easy.					
3s   3p   3d					
S atom in the ground state					
Two unpaired electrons account for an oxidation					
state of $+2$ .					
S atom in the first					
Four unpaired electrons account for an oxidation					
state of +4					
S atom in the second 1 1111 111					

Except oxygen, all the elements have vacant *d*-orbitals in their valence shells. In the ground state, they have only two unpaired electrons which permit formation of two bonds. This explains their 2 oxidation state. In the excited state, however, one of the *p*-electrons goes to the vacant *d*-orbital of the same shell, thus, making 4 unpaired electrons available for chemical bonding. This accounts for +4 oxidation state. Thus, S, Se and Te are tetravalent in their typical compounds

state of +6

with oxygen.

Six unpaired electrons account for an oxidation

On further excitation, the ns-electrons also get unpaired, thus making 6 unpaired electrons available for bond formation. This explains +6 oxidation state. Thus in their compounds with fluorine, these elements exhibit on oxidation state of +6.

The behaviour of oxygen is different. It belongs to the second period and has only two shells, viz. K and L-shells in its structure. Since the outer L-shell contains only s- and p-orbitals, therefore, oxygen does not have d-orbitals in its valence shell. So, in the case of oxygen, the 2p-electrons on excitation have to go to 3s-orbital, there being no d-orbitals in L-shell. But since too much energy is required to excite an electron into a higher shell (in this case from L to M-shell), the electrons in oxygen do not get unpaired. Therefore, oxygen behaves as a divalent element only.

# 3.5 CHEMICAL REACTIVITY

- 1. Oxygen is the most reactive element of the group despite it has high bond dissociation energy of oxygen molecule (493.4 kJ mol<sup>-1</sup>) as nearly all its reactions are exothermic. Once initiated, these reactions continue spontaneously. Oxygen directly combines with almost all the metals except noble metals, all the non-metals except noble gases and halogens and many compounds under suitable conditions. The oxides are generally stable compounds. The elements such as W, Pt, Au, halogens and noble gases which do not directly combine with oxygen, form compounds with oxygen indirectly.
- 2. After oxygen, sulphur is quite reactive element especially at high temperatures which help in breaking of S—S bonds in S<sub>s</sub> molecules. Sulphur burns in air and reacts directly with carbon, phosphorus, arsenic and many metals. Oxidising acids oxidise it into SO2 and alkalies dissolve it to give sulphides and thiosulphates. It reacts with H<sub>2</sub> and halogens. The sulphides are stable compounds and many metals are found in nature in the form of sulphides.
- 3. However, the reactivity of group 16 elements decreases from oxygen to polonium: O > S > Se > Te > Po.
  - Selenium and tellurium combine with highly electropositive elements such as alkali and alkaline earth metals. Se and Te combine with oxygen, fluorine and chlorine. In general, the compounds of selenium and tellurium are less stable than oxygen and sulphur.

# .5.1 REACTIVITY TOWARDS HYDROGEN— FORMATION OF HYDRIDES

the elements of group 16 form hydrides having general formula E; where E = O, S, Se, Te and Po, i.e.  $H_2O$ ,  $H_2S$ ,  $H_2Se$ ,  $H_2Te$ d H<sub>2</sub>Po.

 $\mathrm{H_2O}$  is obtained by burning hydrogen in the atmosphere of ygen, while H<sub>2</sub>S, H<sub>2</sub>Se and H<sub>2</sub>Te are obtained by the action of ids on sulphides, selenides and tellurides.

$$\begin{aligned} & \operatorname{FeS} + \operatorname{H}_2 \operatorname{SO}_4 \longrightarrow \operatorname{FeSO}_4 + \operatorname{H}_2 \operatorname{S} \\ & \operatorname{Na}_2 \operatorname{Se} + \operatorname{H}_2 \operatorname{SO}_4 \longrightarrow \operatorname{Na}_2 \operatorname{SO}_4 + \operatorname{H}_2 \operatorname{Se} \end{aligned}$$

#### 3.5.2 STRUCTURE

All these hydrides have angular shape involving  $sp^3$ -hybridisation of the central atom. The bond angles, however, decrease from H<sub>2</sub>O to H<sub>2</sub>Te.

Hydride	H <sub>2</sub> O	H <sub>2</sub> S	H <sub>2</sub> Se	H <sub>2</sub> Te
Bond angle	104.5°	92.1°	91°	90°

Due to stronger lone pair-lone pair (lp-lp) than bond pair-bond pair (bp-bp) repulsions, the bond angle in water decreases from the tetrahedral value of 109.28° to 104.5°. As we move down the group from O to Te, the size of the central atom goes on increasing and its electronegativity goes on decreasing. As a result, the position of the two bond pairs shifts away and away from the central atom as we move from H<sub>2</sub>O to H<sub>2</sub>Te. Consequently the repulsions between the bond pairs decrease as we move from H<sub>2</sub>O to H<sub>2</sub>Te and, therefore, the bond angle decreases in the same order:

$$H_2O > H_2S > H_2Se > H_2Te$$

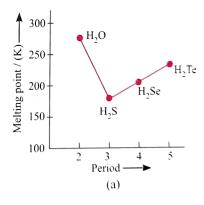
Oxygen forms another important hydride, H<sub>2</sub>O<sub>2</sub>.

The bond angles suggest that in  $H_2S$ ,  $H_2Se$  and  $H_2Te$  the orbitals used for bonding are close to pure p-orbitals.

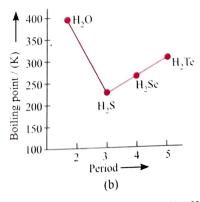
#### 3.5.3 PHYSICAL STATE

Water is colourless, odourless liquid while other hydrides are colourless, poisonous gases with bad odour.

#### 3.5.4 MELTING AND BOILING POINTS



[Melting point:  $H_2O(373) \ge H_2Te(222) \ge H_2Se(208) \ge H_2S(188) K$ ]



[Boiling point:  $H_2O(373) > H_2Te(269) > H_2Se(232) > H_2S(213) K$ ]

Fig. 3.2 (a) Melting and (b) boiling points of hydrides of group 16 elements

Explanation of melting and boiling points of hydrides of group 16 elements.

Melting point	Boiling point
The melting point of $H_2O$ is the highest in the hydrides due to intermolecular H-bonding. The H-bonding in $H_2O$ is	Same explanation as in the melting point.
greater than that of HF and $NH_3$ . Since the EN of $F > O > N$ . But greater H-bonding in $H_2O$ than HF is due to the reason that $H_2O$ forms four H-bonds while HF forms two H-bonds. Hence the increased molecular masses of $H_2$ Te does not affect the melting point of $H_2O$ .	

#### 3.5.5 VOLATILITY

Water has low volatility (high boiling point) as hydrogen bonding brings association.  $H_2S$  has high volatility as no hydrogen bonding is present. Volatility decreases from  $H_2S$  to  $H_2$ Te due to increase in molecular masses of the hydrides.

#### 3.5.6 COVALENT CHARACTER

As the electronegativity difference between E and H decreases, the covalent character of these hydrides increases from  $\rm H_2O$  to  $\rm H_2Te$ . Water molecule is highly polar. It has high dielectric constant and hence acts as an excellent solvent for inorganic compounds.

Covalent character: H<sub>2</sub>O < H<sub>2</sub>S < H<sub>2</sub>Se < H<sub>2</sub>Te

#### 3.5.7 THERMAL STABILITY

The thermal stability decreases as the atomic mass increases. Water dissociates at 2000°C while tellurium hydride,  $\rm H_2Te$ , decomposes at room temperature. This is due to an increase in E–H bond length down the group and hence E–H bond becomes weaker and breaks on heating.

Thermal stability:  $H_2O > H_2S > H_2Se > H_2Te$ 

#### 3.5.8 ACIDIC CHARACTER

This increase in acid strength can be easily explained on the basis of their bond dissociation energy. As the atomic size increases down the group, the bond length increases and hence the bond strength decreases. Consequently, the cleavage of E—H bond (E = O, S, Se, Te, etc.) becomes easier. As a result, the tendency to release hydrogen as proton increases, i.e., acid strength increases down the group. Thus,  $\rm H_2O$  is least acidic while  $\rm H_2Po$  is most acidic.

Acidic character:  $H_2O < H_2S < H_2Se < H_2Te < H_2Po$ 

#### 3.5.9 REDUCING NATURE

Hydrides of all elements of group 16 except that of oxygen, i.e., water act as reducing agents. Their reducing character, however, increases from H<sub>2</sub>S to H<sub>2</sub>Te. This is due to the decrease in their thermal stability. In other words, as the thermal stability decreases, the reducing character increases.

 $\label{eq:Reducing nature:} \quad H_2S < H_2Se < H_2Te$ 

# **3.5.10 BURNING**

 $H_2S$ ,  $H_2Se$ ,  $H_2Te$  and  $H_2Po$  burn in atmosphere of oxygen blue flame forming dioxides.

ue flame forming distributes 
$$2H_2S + 3O_2 \longrightarrow 2H_2O + 2SO_2$$

# 3.5.11 REACTIVITY WITH OXYGEN

All the elements of group 16 form two type of  $oxide_{S_1, i_{\mathbb{Q}}}$  and  $EO_2$  and  $EO_3$  where E = S, Se, Te or Po.

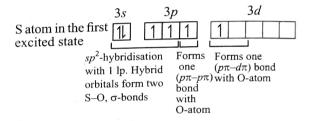
# 3.5.12 DIOXIDES (EO<sub>2</sub>)

**Preparation:** Sulphur, selenium and tellurium when burnt in  $a_{ij}$  form dioxides of the formula  $EO_2$ .

$$S_{8(s)} + 8O_{2(g)} \xrightarrow{\Delta} 8SO_{2(g)}$$

#### Structures

SO<sub>2</sub>: Sulphur dioxide exists as discrete molecules even in the solid state. These molecules are held together by weak  $v_{an}$  der Waals forces of attraction. Therefore, SO<sub>2</sub> is a gas at  $v_{an}$  temperature. In SO<sub>2</sub>, S is  $sp^2$ -hybridised. Two of the three  $sp^2$ -orbitals form two  $\sigma$ -bonds with oxygen atoms while the third contains the lone pair of electrons.



Sulphur is now left with one half-filled p-orbital and one half-filled d-orbital. These form one  $p\pi$ – $p\pi$  double bond and one  $p\pi$ – $d\pi$  double bond with oxygen atoms. Thus, SO<sub>2</sub> has bent (angular structure. Because of bent structure, SO<sub>2</sub> molecule has a dipole moment of 1.63 D.

The actual bond angle is  $119.5^{\circ}$ . Despite the fact that two  $\pi$ -bonds are formed due to overlap of different orbitals, the two S—O bonds are, however, equal (143 pm) because of resonance between two structures (I and II) (Figure 3.3).

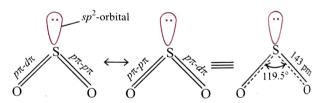


Fig. 3.3 Resonance structures of SO<sub>2</sub>

**Selenium dioxide** is a white crystalline solid. In the gaseous state, it exists as discrete monomeric molecules having structure similar to that of SO<sub>2</sub> [Figure 3.4(a)]. However, in the solid state, it has a non-planar polymeric structure [Figure 3.4 (b)] consisting of infinite chains.

 ${\rm TeO_2}$  and  ${\rm PoO_2}$  are non-volatile crystalline ionic solids and each one of these exists in two crystalline forms.  ${\rm TeO_2}$  in the solid stall has a layered structure consisting of  ${\rm TeO_4}$  units.

The different structures of the dioxides of the elements of group 16 arise due to the fact that the tendency of these elements to form  $p\pi-p\pi$  and  $p\pi-d\pi$  multiple bonds decreases with increase in atomic size down the group  $(\downarrow)$ .

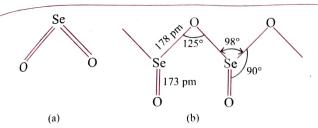


Fig. 3.4 Structures of SeO, (a) in the gas phase and (b) linear chain form of solid SeO,

# 3.5.13 PROPERTIES OF DIOXIDES

1. Acid base character: The dioxides, EO2, differ from one another in their reaction with water.

SO, dissolves in  $H_2O$  giving sulphurous acid ( $H_2SO_2$ ) which exists only in solution and cannot be isolated.

SeO, dissolves giving selenous acid (H<sub>2</sub>SeO<sub>3</sub>) which can be isolated in the crystalline state. TeO<sub>2</sub> is almost insoluble in water. However, it dissolves both in alkalies to form tellurites and in acids to form basic salts. Thus, TeO, is amphoteric in nature. Similarly, PoO, is also amphoteric though more basic in character than TeO<sub>2</sub>. Thus, the acidic character of the dioxides of group 16 elements decreases as on moving down the group from S to Po.

$$SO_2 + H_2O \longrightarrow H_2SO_3$$
 (Sulphurous acid)  
 $SeO_2 + H_2O \longrightarrow H_2SeO_3$  (Selenous acid)

$$TeO_2 + 2NaOH \longrightarrow Na_2TeO_3 + H_2O$$

Sodium tellurite

$$2\text{TeO}_2 + \text{HNO}_3 \longrightarrow 2\text{TeO}_2 \cdot \text{HNO}_3 \text{ or Te}_2\text{O}_3 \cdot (\text{OH})(\text{NO}_3)$$
Basic nitrate

2. Reducing-oxidising properties: Since +6 oxidation state of S is more stable than +4, therefore, it acts as a reducing agent. Further, since the stability of +6 oxidation decreases from S to Te, therefore, the reducing character of the dioxides decreases while their oxidising character increases. Thus, TeO2 acts as an oxidising agent.

#### ILLUSTRATION 3.1

Reducing property of dioxides decreases from SO<sub>2</sub> to TeO<sub>2</sub>.

 $SO_2$  undergoes oxidation to  $SO_4^{2-}$  and thus is reducing.

$$^{4+}$$
SO<sub>2</sub>  $\longrightarrow$   $^{6+}$ SO<sub>4</sub>  $^{2-}$  +  $2e^{\Theta}$ 

ii. TeO2 undergoes reduction to TeO and thus is oxidising or less reducing. This is due to the inert pair effect. Lower O.S. is more stable down the group.

$$2e^{\Theta} + {^{4+}TeO_2} \longrightarrow {^{2+}TeO}$$

### 3.5.14 TRIOXIDES (EO<sub>3</sub>)

All the elements of group 16 form trioxides, EO<sub>3</sub>. O<sub>3</sub> and SO<sub>3</sub> are gases. Sulphur in SO<sub>3</sub> is  $sp^2$ -hybridised. The three  $sp^2$ -orbitals of sulphur overlap with p-orbitals of oxygen to form three S—O,  $\sigma$ -bonds. The sulphur atom is now left with one p- and two d-orbitals which overlap with p-orbitals of oxygen to form three  $\pi$ -bonds. However, due to resonance between the three canonical structures (I, II, III), all the three S—O bond lengths are equal (Figure 3.5).

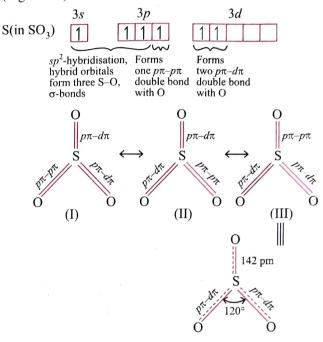


Fig. 3.5 Resonance structures of SO<sub>3</sub>

The molecules of SO3 are held by weak van der Waals forces of attraction. Therefore SO<sub>2</sub> exists as a triangular planar gaseous molecule at room temperature [Figure 3.6(a)] Due to trigonal planar structure, the three S-O dipoles cancel one another. Therefore, the net dipole moment of SO<sub>3</sub> is zero.

However, in the solid state, SO<sub>3</sub> exists in several modifications of which a cyclic trimer [Figure 3.6(b)] or a linear polymeric chain structure [Figure 3.6(c)] are important. SeO<sub>3</sub>, on the other hand, exists as a cyclic tetramer, Se<sub>4</sub>O<sub>1</sub>, in the solid state [Figure 3.6(d)].

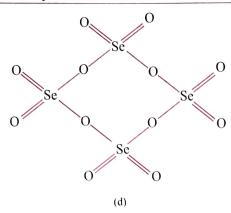


Fig. 3.6 (a) Planar triangular structure of gaseous SO<sub>3</sub>, (b) cyclic trimer of solid  $\mathrm{SO_3}$ , (c) linear chain form of solid  $\mathrm{SO_3}$  and (d) cyclic tetramer of solid SeO<sub>3</sub>

Solid TeO<sub>3</sub> has a network structure in which TeO<sub>6</sub> octahedra share all vertices. All the trioxides are acidic in nature. Acidic nature decreases down the group  $(\downarrow)$  with the decrease in electronegativity of central atom.

$$\begin{array}{ll} \mathrm{SO_3} + \mathrm{H_2O} \longrightarrow \mathrm{H_2SO_4} & \text{(Sulphuric acid)} \\ \mathrm{SeO_3} + \mathrm{H_2O} \longrightarrow \mathrm{H_2SeO_4} & \text{(Selenic acid)} \\ \mathrm{TeO_3} + \mathrm{H_2O} \longrightarrow \mathrm{H_6TeO_6} & \text{(Telluric acid)} \end{array}$$

### 3.5.15 REACTIVITY TOWARDS HALOGENS— FORMATION OF HALIDES

All group 16 elements form compounds with halogens. Since fluorine is more electronegative than oxygen, hence fluorine compounds with oxygen are called fluorides such as oxygen difluoride, OF<sub>2</sub>. On the other hand, oxygen is more eletronegative than chlorine, bromine or iodine, so oxygen derivatives are called oxides such as chlorine dioxide, ClO<sub>2</sub>.

### 3.5.15.1 Some Important Points of Halides

- 1. All the elements form hexafluorides, i.e. fluorine brings out maximum valency of six with these elements due to its small size and highest electronegativity as compared to that of the atoms of the other halogens.
- 2. With the increase in the size of the halogen atom the maximum coordination number of the elements of group 16 decreases. Thus there are no hexachlorides.
- 3. Te<sub>2</sub>Cl<sub>2</sub> and Po<sub>2</sub>Cl<sub>2</sub> are not known because the bond between the two atoms such as Te-Te or Po-Po will be weaker due to their large size. Moreover, chlorine being highly electronegative, will withdraw electrons making Te-Te or Po-Po bond still more weak.
- 4. Generally, the order of thermal stability of the halides of any particular oxidation state decreases in the order:

### 3.5.16 HEXAHALIDES

Only fluorine forms hexafluorides, i.e. fluorine brings out the maximum valency of six with S, Se and Te. SF<sub>6</sub>, SeF<sub>6</sub> and TeF<sub>6</sub> are all formed by direct combination with fluorine, e.g.

$$S + 3F_2 \longrightarrow SF_6$$

All the hexafluorides have octahedral structures, with the central atom (S, Se or Te) being  $sp^3d^2$  hybridised (Figure 3.8)

SF<sub>6</sub> is a colourless, odourless and non-toxic gas at room temperature. It is thermally stable and chemically inert. It chemical inertness is due to the reason that the six F atomy effect by the reasons. protect the sulphur atom from attack by the reagents to such an extent that even thermodynamically most favourable reactions like hydrolysis do not occur. However, as the size of the central atom increases, steric hindrance decreases and hence the hydrolysis becomes easy.

Alternatively, as the size of the atom increases, the electronegativity decreases and the bond polarities increase leading to increase in reactivity or decrease in stability  $d_{0y_0}$ the group. Thus, the order of hydrolysis of hexafluorides is  $SF_6 > SeF_6 > TeF_6$ .

In other words, TeF<sub>6</sub> undergoes hydrolysis readily.

$$TeF_6 + 6H_2O \longrightarrow H_6TeO_6 + 6HF$$

 $\begin{aligned} \text{TeF}_6 + 6\text{H}_2\text{O} &\longrightarrow \text{H}_6\text{TeO}_6 + 6\text{HF} \\ \text{Similarly, TeF}_6 \text{ adds F}^{\circleddash} \text{ to form [TeF}_7]^{\circleddash} \text{ and [TeF}_8]^{2-} \\ \text{ion}_{\mathbb{R}_8} \end{aligned}$ Moreover, TeF<sub>6</sub> reacts with other Lewis bases such as amines in give eight coordinate adducts like [(CH<sub>3</sub>)<sub>3</sub>N]<sub>2</sub>TeF<sub>6</sub>.

All these hexafluorides are colourless gases, which means that they have very low boiling points which indicates a high degree of covalency.

#### 3.5.17 TETRAHALIDES

Many tetrahalides are known: SF<sub>4</sub> is a gas, SeF<sub>4</sub> is a liquid while TeF<sub>4</sub> is a solid. S, Se, Te and Po form tetrachlorides and bromides while Te and Po form tetraiodides. In all tetrahalides the central atom is  $sp^3d$  hybridised with 1 lp and hence possesses trigonal bipyramidal geometry in which one of the equatorial position is occupied by lone pair of electron. This lone pair repels the axial bond pairs thereby decreasing the bond angle from 180° to 173° in SF<sub>4</sub>. Thus SF<sub>4</sub> has see-saw shape.

The tetrahalides can act both as Lewis bases due to the presence of a lone pair of electrons and Lewis acids because the central atom can extend its coordination number to six.

$$SF_4 + BF_3 \longrightarrow (SF_3)(BF_4);$$
  $SF_4 + 2F^{\odot} \longrightarrow [SF_6]^{2-}$   
Lewis base Lewis acid

Further, unlike SF<sub>6</sub> which does not undergo hydrolysis because the six F atoms protect the sulphur atom from attack by water due to steric hindrance.  $SF_4$  readily undergoes hydrolysis because the four F atoms cannot protect the S atom from attack by

$$SF_4 + 2H_2O \longrightarrow 4HF + SO_2$$
;  $SF_6 + H_2O \longrightarrow No$  action

SF<sub>4</sub> readily undergoes hydrolysis due to the presence of vacant 3d orbitals in S, S can expand its coordination number. It is used as a fluorinating agent for many inorganic and organic compounds Just like tetrafluorides, tetrachlorides especially TeCl<sub>4</sub> react with HCl to form complex ions such as  $[TeCl_6]^{2-}$ .

The stability of the tetrahalides increases with increase in polarity of the bonds, i.e.,  $SCl_4 \le SeCl_4 \le TeCl_4$ .

Similarly, the stability of tetrabromides increases from SeBr4 to PoBr<sub>4</sub>.

# 3.5.18 SF<sub>4</sub> AND SeF<sub>4</sub> AS FLUORINATING AGENTS

Both SF<sub>4</sub> and SeF<sub>4</sub> are used as fluorinating agents for the conversion of following groups e.g.,

i. (R—OH) group to (R—F) group. For example

$$H_3C \xrightarrow{[OH]} \xrightarrow{SF_4 \text{ or}} H_3C \xrightarrow{F}$$

$$\begin{array}{c} \text{ii.} \begin{pmatrix} -C = O \end{pmatrix} \text{group to} \begin{pmatrix} -C - F \\ F \end{pmatrix} \text{group. For example} \\ H_3C \\ H_3C + C = O \end{pmatrix} \xrightarrow{SF_4 \text{ or}} H_3C \\ H_3C + C = O \end{pmatrix} \xrightarrow{SF_4 \text{ or}} H_3C + C - F \\ \text{iii.} \begin{pmatrix} -P = O \end{pmatrix} \text{group to} \begin{pmatrix} -P - F \\ F \end{pmatrix} \text{group. For example} \\ HO + F \\ OH \end{pmatrix} \xrightarrow{SF_4 \text{ or}} OH + F \\ OH \\ \text{iv.} \begin{pmatrix} -C = O \\ F \end{pmatrix} \text{group to} \begin{pmatrix} -C - F \\ F \end{pmatrix} \text{group. For example} \\ H_3C + C = O \end{pmatrix} \xrightarrow{SF_4 \text{ or}} R + C - F \\ F \\ \text{v.} \begin{pmatrix} O \\ -C - F \end{pmatrix} \text{group. For example} \\ H_3C + C = O \end{pmatrix} \xrightarrow{SF_4 \text{ or}} H_3C + C - F \\ F \\ \text{group. For example} \\ H_3C + C = O \end{pmatrix} \xrightarrow{SF_4 \text{ or}} H_3C + C - F \\ F \\ \text{group. For example} \\ H_3C + C = O \end{pmatrix} \xrightarrow{SF_4 \text{ or}} H_3C + C - F \\ F \\ \text{group. For example} \\ H_3C + C = O \end{pmatrix} \xrightarrow{SF_4 \text{ or}} H_3C + C - F \\ F \\ \text{group. For example} \\ H_3C + C = O \end{pmatrix} \xrightarrow{SF_4 \text{ or}} H_3C + C - F \\ F \\ \text{group. For example} \\ \text{group. For ex$$

#### 3.5.19 DIHALIDES

All the elements of group 16 except selenium form stable dichlorides and dibromides. Di-iodides are not formed. Dihalides form tetrahedral molecules due to  $sp^3$  hybridisation of central atom. However, due to the presence of two lone pairs of electrons, they have bent structure like water.

In  $SCl_2$ , the bond angle is little smaller (103°) as compared to that in  $H_2O$  (104.5°). This is due to the reason that S is less electronegative than O. As a result, the bond pairs of the two S-Cl bonds lie away from the S atom in  $SCl_2$  as compared to those of O-H bonds in  $H_2O$ . Consequently, bond pair—bond pair repulsions decrease and hence the bond angle decreases to  $103^\circ$  in  $SCl_2$  from  $104.5^\circ$  in  $H_2O$ .

### 3.5.20 MONOCHLORIDES

Dimeric monochlorides such as  $S_2F_2$ ,  $S_2Cl_2$  and  $S_2Br_2$  are known. Their structure is similar to  $H_2O_2$ .

S similar to 
$$H_2O_2$$
.

S  $\frac{202 \text{ pm}}{104^{\circ}}$  S  $\frac{199 \text{ pm}}{104^{\circ}}$  Cl

### ILLUSTRATION 3.2

- **a.** Elements of group 16 generally show lower value of first ionisation enthalpy as compared to the corresponding periods of group 15. Why?
- **b.** H<sub>2</sub>S is less than acidic than H<sub>2</sub>Te. Why?

#### Sol.

- a. Elements of group 16 generally show lower value of first ionisation enthalpy as compared to the corresponding elements of group 15. This is due to the extra stability of half-filled electronic configuration of group 15 elements  $(ns^2np^3)$ , hence more energy is required to remove an electron as compared to those of group 16 elements  $(ns^2np^4)$ .
- b. Down the group (↓), as the size of the element increases, E—H bond length increases and hence E—H bond strength decreases and bond dissociation energy decreases. In other words, H—S bond dissociation energy is more than that of H—Te bond dissociation energy and hence H—S bond ionises less readily than H—Te bond. Therefore, H<sub>2</sub>S is a weaker acid than H<sub>2</sub>Te.

# 3.6 ANOMALOUS BEHAVIOUR OF OXYGEN

Oxygen the first member of group 16 differs from the rest of member due to (a) small size, (b) high EN and (c) non-availability of d-orbitals in the valence shell.

The main points of difference between oxygen and the rest of the members of group 16 are as follows:

- 1. Physical state: Oxygen is a gas at room temperature while other members are solids.
- 2. Atomicity: Oxygen molecule is diatomic (O<sub>2</sub>) while the molecules of the other elements are more complex, e.g., sulphur and selenium have octa-atomic molecules (i.e., S<sub>8</sub> and Se<sub>8</sub>) with puckered ring structures.
- 3. Non-metallic/metallic character: Being highly electronegative (3.5), oxygen is a typical non-metal. Sulphur (EN = 2.5) is also non-metallic but other members of this group exhibit metallic character also.
- 4. Oxidation states: Being most electronegative element of the group, oxygen usually shows an oxidation state of -2 in most of its compounds (except in peroxides, O<sub>2</sub>F<sub>2</sub> and OF<sub>2</sub>). Sulphur also shows an oxidation state of -2 to some extent. Other elements of this group, however, do not show negative oxidation states. Further, oxygen does not have *d*-orbitals. That is why it cannot expand its octet and hence cannot show positive oxidation states. However, other elements of this group have vacant *d*-orbitals in the valence shell and hence can show positive oxidation states of +2, +4 and +6.
- **5. Nature of compounds:** Due to high electronegativity, oxygen is more ionic in its compounds. The dinegative anion (O<sup>2-</sup>) is very common. The dinegative anions of other

elements (i.e., S<sup>2-</sup>, Se<sup>2-</sup>, Te<sup>2-</sup>) are less common. In other words, compounds of oxygen are ionic as well as covalent while those of sulphur and other members of this group are mostly covalent.

- 6. Multiple bonds: Due to small size and high electronegativity, oxygen forms  $p\pi$ – $p\pi$  multiple bonds with elements having similar size, i.e., carbon, nitrogen (C = O, C = N, C = N), etc. This tendency of forming multiple bonds is not shown by other elements of this group mainly due to larger size and lower electronegativity.
- 7. Hydrogen bonding: Due to high electronegativity, oxygen forms H-bonds. For example, the hydride of oxygen (H<sub>2</sub>O) forms intermolecular H-bonds while hydrides of other elements of this group (H<sub>2</sub>S, H<sub>2</sub>Se, etc.) do not. As a result, H<sub>2</sub>O is a liquid at room temperature while hydrides of other elements are gases.
- 8. Magnetic nature: Due to the presence of two unpaired electrons, O2 is paramagnetic in gaseous, liquid and solid states. The other elements of this group are however, diamagnetic.

# 3.7 DIOXYGEN

Priestley and Scheele obtained oxygen by heating suitable oxygen compounds. Scheele called it vital air or fire air. Lavoisier regarded it as an essential constituent of all acids and named it oxygen (oxus = acid, gennas = maker).

#### 3.7.1 LABORATORY PREPARATION

The usual laboratory method is of heating a mixture of potassium chlorate and manganese dioxide in the ratio of 4:1. KClO<sub>2</sub> evolves oxygen at 375°C. At this temperature, it melts and gets converted into potassium perchlorate which decomposes at higher temperature to evolve oxygen. When MnO2 is added, it starts giving oxygen at 250°C. Here MnO<sub>2</sub> acts as a catalyst.

$$\begin{array}{c} 4\text{KClO}_{3} \longrightarrow 3\text{KClO}_{4} + \text{KCl} \\ \text{Potassium} & \text{Potassium} \\ \text{chlorate} & \text{perchlorate} \end{array}$$

$$KClO_4 \xrightarrow{650^{\circ}C} KCl + 2O_2$$

MnO2 used for this purpose should be completely free from carbon as KClO<sub>2</sub> and carbon mixture is explosive in nature. The mixture should be first heated gently and then strongly when it is ensured that there is no vigorous reaction.

#### 3.7.2 COMMERCIAL METHODS

The main sources for large-scale preparation of dioxygen are air and water.

From liquid air: The most economical method for commercial preparation of dioxygen involves liquefaction of air (after removing CO<sub>2</sub> and water vapours) followed by fractional distillation of the liquid air thus obtained. During this process, dinitrogen (N<sub>2</sub>) with lower boiling point (77 K) distils over in the gaseous form leaving behind dioxygen with higher boiling point (90 K) in the liquid state.

# 3.8 PHYSICAL AND CHEMICAL PROPERTIES OF OXYGEN

# 3.8.1 Physical Properties

- 1. a. Oxygen is a colourless, odourless and tasteless gas
  - b. Liquid dioxygen is pale blue in colour, and the soliding also blue. The colour arises due to electronic transitions which excite the ground state (triplet state) to a singlet state. This transition is forbidden in gaseous  $dioxyge_{\eta}$ In liquid or solid  $O_2$ , a single photon may collide  $w_{\text{With}}$ two molecules simultaneously and promote both the molecules to excited states, absorbing red-yellow-green light, so O<sub>2</sub> appears blue.

Second excited state (electrons have opposite spins)

Singlet

First excited state (electrons are paired)

Singlet

þ

is

Ground state (electrons have parallel spins)



- 2. Liquefies at 90 K and freezes at 55 K.
- 3. Despite having even number of electrons, oxygen is paramagnetic. This can be explained on the basis of molecular orbital diagram for O2 molecule (Figure 2.78 (Part 1)).

### 3.8.2 Chemical Properties

The bond dissociation energy of dioxygen is high (493.4 & mol<sup>-1</sup>) and hence the reactions of dioxygen require initiation by external heating. However, when the reaction starts, it continues on its own. This is due to the reason that the chemical reactions of dioxygen are exothermic and the heat liberated during the reaction is sufficient to carry on the reactions.

#### 3.8.2.1 Some Important Chemical Properties

#### Reactions of Oxygen

i. 
$$4Na_{(s)} + O_{2(g)} \longrightarrow 2Na_2O_{(s)}$$

ii. 
$$2Na_{(s)} + O_{2(g)} \xrightarrow{-575 \text{ K}} Na_2O_{2(s)}$$

iii. 
$$2Mg_{(s)} + O_{2(g)} \xrightarrow{\text{Heat}} 2MgO_{(s)}$$

iv. 
$$4Al_{(s)} + 3O_{2(g)} \xrightarrow{\text{Heat}} 2Al_2O_{3(s)}$$

v. 
$$4Fe_{(s)} + 3O_{2(g)} \xrightarrow{\text{Heat}} 2Fe_2O_{3(s)}$$

v. 
$$4Fe_{(s)} + 3O_{2(g)} \xrightarrow{\text{Heat}} 2Fe_2O_{3(s)}$$
  
vi.  $2H_{2(g)} + O_{2(g)} \xrightarrow{\text{or Electric discharge}} 2H_2O_{(g)}$ 

vii. 
$$N_{2(g)} + O_{2(g)} \xrightarrow{3300 \text{ K}} 2NO_{(g)}$$

This reaction occurs in the atmosphere, when lightning occurs in the sky.

ix. 
$$2C_{(s)} + O_{2(g)} \xrightarrow{\text{Heat}} 2CO_{(g)}$$
(Carbon monoxide)

$$\begin{array}{c} \textbf{x.} \ C_{(8)} + O_{2(g)} \xrightarrow{\text{Heat}} CO_{2(g)} \\ \text{(Excess)} & \text{(Carbon dioxide)} \\ \textbf{xi.} \ P_{4(s)} + 5O_2 \longrightarrow P_4O_{10(s)} \\ \textbf{xii.} \ 2SO_{2(g)} + O_{2(g)} \xrightarrow{\phantom{=}} \frac{723 \text{ K 2 atm}}{\text{Pt or V}_2O_5} 2SO_{3(g)} \\ \textbf{xiii.} \ 4HCl_{(g)} + O_{2(g)} \xrightarrow{\phantom{=}} \frac{700 \text{ K, CuCl}_2}{\text{Pt or V}_2O_5} 2H_2O_{(g)} + Cl_{2(g)} \\ \textbf{xiv.} \ 4NH_{3(g)} + 5O_{2(g)} \xrightarrow{\phantom{=}} \frac{1100 \text{ K, Pt}}{\text{4NO}_{(g)}} 4NO_{(g)} + 6H_2O_{(g)} \\ \textbf{xv.} \ CH_{4(g)} + 2O_{2(g)} \longrightarrow CO_{2(g)} + 2H_2O_{2(g)} \\ \text{Methane} \qquad \Delta_c H^{\Theta} = -890 \text{ kJ mol}^{-1} \\ \textbf{xvii.} \ CH_2 = CH_{2(g)} + 3O_{2(g)} \longrightarrow 2CO_{2(g)} + 2H_2O_{(g)} \\ \text{Ethene} \qquad \Delta_c H^{\Theta} = -1411 \text{ kJ mol}^{-1} \\ \textbf{xvii.} \ CS_{2(g)} + 3O_{2(g)} \xrightarrow{\phantom{=}} \frac{\text{Heat}}{\text{4}} CO_{2(g)} + 2SO_{2(g)} \\ \textbf{xviii.} \ 2ZnS_{(s)} + 3O_{2(g)} \xrightarrow{\phantom{=}} \frac{\text{Heat}}{\text{4}} 2ZnO_{(s)} + 2SO_{2(g)} \\ \textbf{xix.} \ 2HgS_{(s)} + 3O_{2(g)} \xrightarrow{\phantom{=}} \frac{\text{Heat}}{\text{4}} 2HgO_{(s)} + 2SO_{2(g)} \\ \textbf{xx.} \ 3O_2 \xrightarrow{\phantom{=}} \frac{\text{Silent electric discharge}}{\text{2}} 2O_3 \\ \text{Priorwises.} \end{array}$$

#### Uses:

- 1. Liquid oxygen is an important constituent of fuels used in
- 2. Oxygen is used for production of oxyhydrogen or oxyacetylene flames which are employed for cutting and welding purposes.
- 3. Oxygen mixed with helium or carbon dioxide is used for artificial respiration.
- 4. Oxygen is used in the manufacture of large number of compounds such as phenol, ethylene oxide, sulphur dioxide, sulphuric acid, nitric acid, chlorine, etc.
- 5. Liquid oxygen mixed with finely divided carbon acts like a dynamite in coal mining.
- **6.** Oxygen is used as an oxidising agent in several reactions.
- 7. <sup>18</sup>O is used as a tracer in the study of tracer mechanisms.

# 3.9 OZONE OR TRIOXYGEN (O<sub>3</sub>)

### 3.9.1 INTRODUCTION

In 1758, Van Marum observed a rotten smell when an electric discharge was passed through air. In 1840, Schonbien attributed that the rotten smell was due to formation of a new gas which he named ozone. The name ozone comes from the Greek word ozo meaning smell. In 1866, Sorret established its formula, O<sub>3</sub>, and pointed out that the ozone is an allotrope of oxygen.

## 3.9.2 PREPARATION

Ozone is prepared by passing a silent electric discharge through pure, cold and dry dioxygen in a specially designed apparatus called the **ozoniser**. During this reaction, conversion of  $\boldsymbol{O}_2$  to ozone is 10% and the product is called ozonised oxygen.

30<sub>2(g)</sub> Silent electric discharge 
$$\simeq 20_{3(g)}$$
;  
 $\Delta_r H^{\Theta} (298 \text{ K}) = +142 \text{ kJ mol}^{-1}$ 

Since the formation of ozone from oxygen is endothermic process, hence it is necessary to use a silent electric discharge (sparkless electric discharge) in its preparation. A silent electric discharge produces less heat and thus prevents the decomposition of ozone back to oxygen.

If concentration of ozone greater than 10% is required, a battery of ozonisers is used and the pure ozone (b.p. 161 K) can be condensed in a vessel surrounded by liquid oxygen.

#### 3.9.3 STRUCTURE OF OZONE

The central oxygen atom in ozone is  $sp^2$ -hybridised containing a lone pair of electrons. As a result, ozone has an angular structure with a bond angle of 117° as shown in Figure 3.7.



Fig. 3.7 Structure of ozone

It is actually a resonance hybrid of the following two resonating structures (I and II) as shown in figure 3.8.

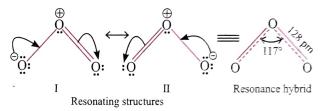


Fig. 3.8 Resonance structure of ozone

Because of resonance, both the oxygen—oxygen bonds have partial double bond character. In other words, both the oxygen—oxygen bonds are equal (128 pm) and lie in between those of oxygen—oxygen double bond length of 110 pm and oxygen—oxygen single bond length of 148 pm.

#### 3.9.4 PHYSICAL PROPERTIES

- 1. When cooled in liquid air, pure ozone condenses to a deep blue liquid (boiling point 161 K) and then to a violet-black solid (melting point 80 K).
- 2. It is about 1.67 times heavier than air because its vapour density (V.D.) is 24 while that of air is 14.4.
- 3. Ozone is a pale blue gas having a strong characteristic smell. In small concentration, it is harmless. However, if the concentration rises above 100 parts per million (ppm). breathing becomes uncomfortable resulting in headache and nausea.
- 4. It is slightly soluble in water but readily dissolves in organic solvents such as turpentine oil, cinnamon oil, carbon tetrachloride, glacial acetic acid, etc.
- 5. Ozone is diamagnetic while dioxygen is paramagnetic.

#### 3.9.5 CHEMICAL PROPERTIES

- 1. Neutral character: Ozone is neutral to litmus.
- 2. Decomposition: Ozone is thermodynamically unstable as compared to oxygen since its decomposition into oxygen

results in liberation of heat ( $\Delta H$  is -ve) and an increase in entropy ( $\Delta S$  is +ve). These two factors reinforce each other, resulting in large negative Gibbs free energy change ( $\Delta G$ ) for the decomposition of ozone to oxygen. Therefore, high concentration of ozone can be dangerously explosive.

Even at ordinary temperature, it decomposes slowly to give oxygen. However, when heated to 473 K or in presence of a catalyst such as manganese dioxide, platinum or cupric oxide, the decomposition takes place rapidly.

$$2O_{3(g)} \xrightarrow{473 \text{ K or catalyst}} 3O_{2(g)}$$
Ozone Dioxyger

3. Oxidising: Ozone is a powerful oxidising agent, second only to F<sub>2</sub> but much stronger than dioxygen. This is due to the reason that ozone has higher energy content than dioxygen and hence decomposes to give dioxygen and atomic oxygen.

$${\rm O}_{3(g)} {\,\longrightarrow\,} {\rm O}_{2(g)} \ + \ {\rm O}_{(g)}$$

Ozone Dioxygen Atomic oxygen

The atomic oxygen thus liberated brings about the oxidation while molecular oxygen is set free.

#### Ionic equation in acidic medium:

$$O_3 + 2H^{\oplus} + 2e^{\Theta} \longrightarrow O_2 + H_2O$$

#### Ionic equation in basic medium:

$$O_3 + H_2O + 2e^{\Theta} \longrightarrow O_2 + 2OH$$

Some important reactions of O<sub>3</sub> are

**a.** It oxidises (PbS to white PbSO<sub>4</sub>) and also sulphides of Cu, Zn and Cd to their respective sulphates

$$O_{3(g)} \longrightarrow O_{2(g)} + O_{(g)}] \times 4$$
  
 $PbS_{(s)} + 4O_{(g)} \longrightarrow PbSO_{4(s)}$ 

$$PbS_{(s)} + 4O_3 \longrightarrow PbSO_{4(s)} + 4O_{2(g)}$$

#### Ionic equation:

It oxidises 
$$(S^{2-} \longrightarrow SO_4^{2-} + 8e^{\Theta})$$
  
 $[O_3 + 2H^{\oplus} + 2e^{\Theta} \longrightarrow O_2 + H_2O] \times 4$   
 $S^{2-} + 4H_2O \longrightarrow SO_4^{2-} + 8H^{\oplus} + 8e^{\Theta}$ 

$$4O_3 + S^{2-} \longrightarrow 4O_2 + SO_4^{2-}$$

**b.** It oxidises HX to corresponding  $X_2$ 

$$O_{3(g)} \longrightarrow O_{2(g)} + O_{(g)}$$

$$2HCl_{(aq)} + O_{(g)} \longrightarrow Cl_{2(g)} + H_2O_{(l)}$$

$$2HCl_{(aq)} + O_3 \longrightarrow Cl_{2(g)} + H_2O_{(l)} + O_{2(g)}$$

**Ionic equation:** It oxidises  $(X^{\Theta} \text{ to } X_2)$  (X = Cl, Br, I) $(2X^{\Theta} \longrightarrow X_2 + 2e^{\Theta})$ 

$$O_3 + 2H^{\oplus} + 2e^{\ominus} \longrightarrow O_2 + H_2O$$
  
 $2Cl^{\ominus} \longrightarrow Cl_2 + 2e^{\ominus}$ 

$$O_3 + 2H^{\oplus} + Cl_2 \longrightarrow O_2 + H_2O + Cl_2$$

c. It oxidises moist KI to  $I_2$  ( $I^{\odot} \longrightarrow I_2$ )

$$O_{3(g)} \longrightarrow O_{2(g)} + O_{(g)}$$

$$2KI_{(aq)} + H_2O_{(l)} + O_{(g)} \longrightarrow 2KOH_{(aq)} + I_{2(s)}$$

$$2KI_{(aq)} + H_2O_{(l)} + O_{3(g)} \longrightarrow 2KOH_{(aq)} + I_{2(s)} + O_{2(g)}$$

#### Ionic equation:

$$O_3 + 2H^{\oplus} + 2e^{\ominus} \longrightarrow O_2 + H_2O$$
  
 $2I^{\ominus} \longrightarrow I_2 + 2e^{\ominus}$ 

$$O_3 + 2H^{\oplus} + 2I^{\bigodot} \longrightarrow O_2 + H_2O + I_2$$

**d.** It oxidises  $NO_2^{\ominus}$  to  $NO_3^{\ominus}$ 

$$O_{3(g)} \longrightarrow O_{2(g)} + O_{(g)}$$

$$KNO_{2(aq)} + O_{(g)} \longrightarrow KNO_{3(aq)}$$

$$KNO_{2(aq)} + O_{3(g)} \longrightarrow KNO_{3(aq)} + O_{2(g)}$$

**Ionic equation:** It oxidises  $(NO_2^{\ominus} \longrightarrow NO_3^{\ominus} + 2e^{\ominus})$   $O_3 + 2H^{\oplus} + 2e^{\ominus} \longrightarrow O_2 + H_2O$  $H_2O + NO_2^{\ominus} \longrightarrow NO_3^{\ominus} + 2H^{\oplus} + 2e^{\ominus}$ 

$$\frac{\text{H}_2\text{O} + \text{NO}_2^{\ \Theta} \longrightarrow \text{NO}_3^{\ \Theta} + 2\text{H}^{\ \Theta} + 2e^{\ \Theta}}{\text{O}_3 + \text{NO}_2^{\ \Theta} \longrightarrow \text{O}_2 + \text{NO}_3^{\ \Theta}}$$

e. It oxidises Fe<sup>2+</sup> salts to Fe<sup>3+</sup> salts

$$O_{3(g)} \longrightarrow O_{2(g)} + O_{(g)}$$

$$2FeSO_{4(aq)} + H_2SO_{4(aq)} + O_{(g)} \longrightarrow Fe_2(SO_4)_{3(aq)} + H_2O_{(g)}$$

$$2\text{FeSO}_{4(\text{aq})} + \text{H}_2\text{SO}_{4(\text{aq})} + \text{O}_{3(g)} \longrightarrow \text{Fe}_2(\text{SO}_4)_{3(\text{aq})} + \text{O}_{2(g)} \\ \text{H}_2\text{O}_{(l)}$$

Ionic equation:  $(Fe^{2^+} \longrightarrow Fe^{3^+} + e^{\bigcirc})$ 

$$O_3 + 2H^{\oplus} + 2e^{\ominus} \longrightarrow O_2 + H_2O$$
  
 $[Fe^{2+} \longrightarrow Fe^{3+} + e^{\ominus}] \times 2$ 

$$O_3 + 2H^{\oplus} + 2Fe^{2+} \longrightarrow O_2 + H_2O + 2Fe^{3+}$$

**f.** It oxidises  $Fe(CN)_6^{4-}$  salts to  $Fe(CN)_6^{3-}$  salts

$$O_{3(g)} \longrightarrow O_{2(g)} + O_{(g)}$$

$$2K_{4}[Fe(CN)_{6}]_{(aq)} + H_{2}O_{(1)} + O_{(g)} \longrightarrow 2K_{3}[Fe(CN)_{6}]_{(aq)} + 2KOH_{(aq)}$$

$$\frac{2K_{4}[Fe(CN)_{6}]_{(aq)} + H_{2}O_{(1)} + O_{3(g)} \longrightarrow 2K_{3}[Fe(CN)_{6}]_{(aq)}}{+ 2KOH_{(aq)} + O_{2(g)}}$$

Ionic equation: 
$$[Fe(CN)_6]^4 \longrightarrow [Fe(CN)_6^3 + e^{\Theta}]$$
  
 $O_3 + 2H^{\oplus} + 2e^{\Theta} \longrightarrow O_2 + H_2O$ 

$$[[Fe(CN)_6]^4 \longrightarrow [Fe(CN)_6]^{3-} + e^{\Theta}] \times 2$$

$$O_3 + 2H^{\oplus} + 2[Fe(CN)_6]^{4-} \longrightarrow O_2 + H_2O + 2[Fe(CN)_6]^{3-}$$

**g.** It oxidises  $MnO_4^{\Theta}$  (green) to  $MnO_4^{2-}$  (pink-violet) in basic medium (used as test for ozone)

$$O_{3(g)} \longrightarrow O_{2(g)} + [O]_{(g)}$$

$$2K_2MnO_{4(aq)} + H_2O_{(1)} + [O]_{(g)} \longrightarrow 2KMnO_{4(aq)} + 2KOH_{(aq)}$$

$$2K_2MnO_{4(aq)} + H_2O_{(1)} + O_{3(g)} \longrightarrow 2KMnO_{4(aq)} + 2KOH + O_{2(g)}$$

#### Ionic equation:

$$O_3 + H_2O + 2e^{\Theta} \longrightarrow O_2 + 2OH^{\Theta}$$

$$[\mathsf{MnO_4}^2 \xrightarrow{2-} \mathsf{MnO_4}^{\ominus} + e^{\ominus}] \times 2$$

$$O_3 + 2MnO_4^{2-} + H_2O \longrightarrow O_2 + 2OH + 2MnO_4^{\Theta}$$

# 3,9.6 QUANTITATIVE ESTIMATION OF O3

When  $O_3$  reacts with an excess of KI solution buffered with a borate buffer (pH = 9.2),  $I_2$  is liberated which can be titrated against a standard solution of  $Na_2S_2O_3$  (sodium thiosulphate). This is a quantitative method of estimation of  $O_3$  gas.

1. Ionic equation of  $O_3$  and  $I^{\Theta}$  ion in basic medium (pH = 9.2)

is
$$2e^{\Theta} + H_2O_{(1)} + O_{3(g)} \longrightarrow O_{2(g)} + H_2O_{(1)} + 2\overset{\Theta}{O}H_{(aq)}$$

$$OR$$

$$2e^{\Theta} + 2H_2O_{(1)} + O_{3(g)} \longrightarrow O_{2(g)} + 2\overset{\Theta}{O}H_{(aq)}$$

$$2l^{\Theta}_{(aq)} \longrightarrow I_{2(s)} + 2e^{\Theta}$$

$$2l^{\Theta}_{(aq)} + H_2O_{(1)} + O_{3(g)} \longrightarrow O_{2(g)} + I_{2(s)} + 2\overset{\Theta}{O}H_{(aq)}$$

2. Ionic equation of liberated  $I_2$  with standard  $Na_2S_2O_3$  in basic medium (pH = 9.2)

$$I_{2(s)} + 2e^{\Theta} \longrightarrow 2I_{(aq)}^{\Theta}] \times 4$$

$$S_2O_3^{2-} + 10\overset{\Theta}{OH}_{(aq)} \longrightarrow 2SO_4^{2-} + 5H_2O + 8e^{\Theta}$$

$$4I_{2(g)} + S_2O_3^{2-} + 10\overset{\Theta}{OH}_{(aq)} \longrightarrow 8I_{(aq)}^{\Theta} + 2SO_4^{2-} + 5H_2O$$

### 3.9.7 OXIDATION OF NON-METALS

Ozone oxidises non-metals like phosphorous, sulphur and iodine to their corresponding oxyacids. For example,

1. It oxidises moist phosphorous to phosphoric acid or phosphate ion

$$[O_{3} \longrightarrow O_{2} + [O]] \times 10$$

$$P_{4} + 6H_{2}O + 10 [O] \longrightarrow 4H_{3}PO_{4}$$

$$P_{4} + 10O_{3} + 6H_{2}O \longrightarrow 4H_{3}PO_{4} + 10 O_{2}$$
Ionic equation:  $(P_{4} \longrightarrow 4PO_{4}^{4-} + 20e^{\Theta})$ 

$$[O_{3} + 2H^{\oplus} + 2e^{\Theta} \longrightarrow O_{2} + H_{2}O] \times 10$$

$$P_{4} + 16H_{2}O \longrightarrow 4PO_{4}^{3-} + 32H^{\oplus} + 20e^{\Theta}$$

$$10O_{3} + 6H_{2}O + P_{4} \longrightarrow 10O_{2} + 4PO_{4}^{3-} + 12H^{\oplus}$$

2. It oxidises moist sulphur to sulphuric acid or sulphate ion

$$[O_{3} \longrightarrow O_{2} + [O]] \times 24$$

$$S_{8} + 24[O] + 8H_{2}O \longrightarrow 8H_{2}SO_{4}$$

$$S_{8} + 24O_{3} + 8H_{2}O \longrightarrow 8H_{2}SO_{4} + 24O_{2}$$

$$Ionic equation: (S_{8} \longrightarrow 8SO_{4}^{2-} + 48e^{\Theta})$$

$$[O_{3} + 2H^{\oplus} + 2e^{\Theta} \longrightarrow O_{2} + H_{2}O] \times 24$$

$$S_{8} + 32H_{2}O \longrightarrow 8SO_{4}^{2-} + 64H^{\oplus} + 48e^{\Theta}$$

$$24O_{3} + S_{8} + 8H_{2}O \longrightarrow 8SO_{4}^{2-} + 16H^{\oplus} + 24O_{2}$$

3. It oxidises moist iodine to iodic acid or iodate ion

$$[O_3 \longrightarrow O_2 + [O]] \times 5$$

$$I_2 + 5[O] + H_2O \longrightarrow 2HIO_3$$

$$I_2 + 5O_3 + H_2O \longrightarrow 2HIO_3 + 5O_2$$

Ionic equation: 
$$(I_2 \longrightarrow 2IO_3^{\ominus} + 10e^{\ominus})$$
  
 $[O_3 + 2H^{\oplus} + 2e^{\ominus} \longrightarrow O_2 + H_2O] \times 5$   
 $I_2 + 6H_2O \longrightarrow 2IO_3^{\ominus} + 12H^{\oplus} + 10e^{\ominus}$   
 $5O_3 + I_2 + H_2O \longrightarrow 2IO_3^{\ominus} + 5O_2 + 2H^{\oplus}$ 

### 3.9.8 OXIDATION OF METALLOIDS

Ozone also oxidises metalloids like As to its corresponding oxyacid. (arsenate ion)

$$[O_{3} \longrightarrow O_{2} + [O]] \times 5$$

$$2As + 5[O] + 3H_{2}O \longrightarrow 2H_{3}AsO_{4}$$

$$2As + 5O_{3} + 3H_{2}O \longrightarrow 2H_{3}AsO_{4} + 5O_{2}$$

$$Ionic equation: (As \longrightarrow AsO_{4}^{3-} + 5e^{\Theta})$$

$$[O_{3} + 2H^{\oplus} + 2e^{\Theta} \longrightarrow O_{2} + H_{2}O] \times 5$$

$$As + 4H_{2}O \longrightarrow AsO_{4}^{3-} + 8H^{\oplus} + 5e^{\Theta}] \times 2$$

$$5O_{3} + 2As + 3H_{2}O \longrightarrow 2AsO_{4}^{3-} + 5O_{2} + 6H^{\oplus}$$

### 3.9.9 OXIDATION OF METALS

Ozone also oxidises certain metals like silver, mercury, copper, etc. to their corresponding oxides. For example,

1. Silver is oxidised to silver oxide (Ag<sub>2</sub>O)

$$[O_{3(g)} \longrightarrow O_{2(g)} + [O]]_{(g)}$$

$$2Ag_{(s)} + O_{(g)} \longrightarrow Ag_2O_{(s)}$$

$$2Ag_{(s)} + O_{3(g)} \longrightarrow Ag_2O_{(s)} + O_{2(g)}$$

$$Ionic equation: (Ag \longrightarrow Ag^{\oplus} + e^{\ominus})$$

$$[O_3 + 2H^{\oplus} + 2e^{\ominus} \longrightarrow O_2 + H_2O$$

$$[Ag \longrightarrow Ag^{\oplus} + e^{\ominus}] \times 2$$

$$O_3 + 2H^{\oplus} + 2Ag \longrightarrow O_2 + H_2O + 2Ag^{\oplus}$$

2. Mercury is oxidised to mercurous oxide (Hg<sub>2</sub>O)

$$O_{3(g)} \longrightarrow O_{2(g)} + [O]_{(g)}$$

$$2Hg_{(l)} + [O]_{(g)} \longrightarrow Hg_2O_{(s)}$$

$$O_{3(g)} + 2Hg_{(l)} \longrightarrow O_{2(g)} + Hg_2O_{(s)}$$
Ionic equation:  $(2Hg \longrightarrow Hg_2^{2+} + 2e^{\Theta})$ 

$$O_3 + 2H^{\oplus} + 2e^{\Theta} \longrightarrow O_2 + H_2O$$

$$2Hg \longrightarrow Hg_2^{2+} + 2e^{\Theta}$$

$$O_3 + 2H^{\oplus} + 2Hg \longrightarrow O_2 + H_2O + Hg_2^{2+}$$

$$O_3 + 2H^{\oplus} + 2Hg \longrightarrow O_2 + H_2O + Hg_2^{2+}$$

The mercurous oxide thus formed dissolves in mercury which loses its meniscus and starts sticking to the glass. This is called **tailing of mercury**. The meniscus can, however, be restored by shaking it with water which dissolves mercurous oxide. This reaction is used as a test of ozone.

3. Exceptional behaviour: In all the oxidation reactions discussed above, the oxidation is brought about by the atomic oxygen and dioxygen is always evolved. However during the oxidation of SO<sub>2</sub> to SO<sub>3</sub> and SnCl<sub>2</sub> in presence of conc. HCl to SnCl<sub>4</sub> the ozone is utilised as a whole and dioxygen is not evolved. Thus,

a. 
$$3SO_{2(g)} + O_{3(g)} \longrightarrow 3SO_{3(g)}$$
  
Sulphur dioxide Sulphur trioxide

**b.** 
$$3\operatorname{SnCl}_{2(s)} + 6\operatorname{HCl}_{(\operatorname{conc.})} + \operatorname{O}_{3(g)} \longrightarrow 3\operatorname{SnCl}_{4(\operatorname{aq})} + 3\operatorname{H}_2\operatorname{O}_{(1)}$$
  
Stannous chloride Stannic chloride

**4. Bleaching action:** Due to its oxidising action, ozone acts as a mild bleaching agent and bleaches vegetable colouring matter.

Vegetable colouring matter  $+ O_3 \longrightarrow$ Colourless oxidised matter  $+ O_3$ 

Ozone also acts as indigo, ivory, litmus, delicate fabrics like silk, wool, etc.

v. Reducing agent: Although ozone is an extremely powerful oxidising agent yet in some reactions, it acts as a weak reducing agent. For example, it reduces peroxides such as hydrogen peroxide, barium peroxide, etc. liberating dioxygen.

i. 
$$H_2O_{2(aq)} + O_{3(g)} \longrightarrow H_2O_{(1)} + 2O_{2(g)}$$

#### Ionic equation:

$$O_3 + 2H^{\oplus} + 2e^{\ominus} \longrightarrow O_2 + H_2O$$

$$H_2O_2 \longrightarrow 2H^{\oplus} + O_2 + 2e^{\ominus}$$

$$H_2O_2 + O_3 \longrightarrow 2O_2 + H_2O$$

ii. 
$$BaO_{2(s)} + O_{3(g)} \longrightarrow BaO_{(s)} + 2O_{2(g)}$$

#### 3.9.10 USES OF OZONE

- 1. As a bleaching agent for oils, flour, ivory, wax and delicate fabrics.
- 2. In the manufacture of artificial silk, synthetic silk, synthetic camphor and potassium permanganate (by oxidation of potassium manganate).
- 3. In destroying odours that arise from cold storage rooms, kitchens of big hotels or slaughter houses.
- **4.** It is used for detecting the position of double bond in the unsaturated organic compounds.
- 5. As a germicide and disinfectant for sterilising water and improving the atmosphere of crowded places like tube railways, mines and cinema halls.

# 3.10 ALLOTROPIC FORMS OF SULPHUR

Sulphur exists in several allotropic forms which may be classified into the following three categories as discussed below:

1. Homocyclic species containing 6–20 sulphur atoms: Several allotropic forms of sulphur containing 6–20 sulphur atoms per ring have been synthesised in the past two decades. Two important allotropes of this category are yellow rhombic (α-sulphur) and monoclinic (β-sulphur). The stable form at room temperature is rhombic sulphur which gets converted into monoclinic sulphur when heated above 369 K.

The method of preparation and properties of these two allotropes are described below:

a. Rhombic or orthorhombic sulphur or octahedral sulphur or  $\alpha\text{-sulphur}$ 

**Preparation.** It is prepared by slowly evaporating the solution of sulphur in  $CS_2$  in a china dish when octahedral crystals of rhombic sulphur appear.

#### **Properties:**

- i. This is the most stable form of sulphur at room temperature while all other varieties of sulphur gradually change into this form on standing.
- ii. It is pale yellow in colour.
- iii. It is insoluble in water but dissolves to some extent in benzene, alcohol and ether. It is readily soluble in CS<sub>2</sub>.
- iv. It has little thermal and electrical conductivity.
- v. Its specific gravity is 2.06 g cm<sup>-3</sup> and melts at 385.8 K.
- vi. It is a crystalline variety and consists of  $S_8$  structural units packed together into octahedral shape (Refer Figure 3.1).
- vii. When heated above 96°C, rhombic sulphur changes into monoclinic sulphur.
- b. Monoclinic sulphur or  $\beta\text{-sulphur}$  or prismatic sulphur:

**Preparation:** It is prepared by melting sulphur in a china dish. The molten sulphur is allowed to cool till a crust is formed. Two holes are made in the crust and the remaining liquid is poured out. On removing, the crust, needle-shaped crystals of monoclinic sulphur separate out.

#### **Properties:**

- It is dull yellow in colour and is soluble in CS<sub>2</sub> but insoluble in H<sub>2</sub>O.
- ii. It has a specific gravity of 1.98 g cm<sup>-3</sup> and melts at 393 K.
- iii. It is stable only above 369 K (or 96°C). Below this temperature, it slowly changes into rhombic sulphur. Thus, at 369 K, both the varieties of sulphur coexist and this temperature is called the **transition temperature**.

Rhombic sulphur  $\frac{> 369 \text{ K}}{< 369 \text{ K}}$  Monoclinic sulphur

**Structure:** Both orthorhombic and monoclinic forms of sulphur are molecular solids which consist of  $S_{\S}$  puckered (non-planar) rings having crown shape. The two forms, however, differ in the manner of packing of the molecules in the crystal lattice.

c. Cyclo-S<sub>6</sub> form: Another important allotropic form of this category is cyclo-S<sub>6</sub> (Engel's sulphur or ∈-sulphur) in which the six membered ring adopts the chair form as shown in figure 3.9.

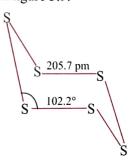


Fig. 3.9 Structure of cyclo-S<sub>6</sub> allotropic form of sulphur

2. Different chain polymers known as catena  $S_n$  sulphur. The most important allotrope of this category is plastic sulphur or γ-sulphur.

Preparation: It is obtained by pouring molten sulphur into cold water when a soft rubber like mass called plastic sulphur

#### **Properties:**

- It does not have a sharp melting point.
- ii. It is an amorphous form of sulphur. It is soft and elastic like rubber in the beginning but hardens on standing and cooling and gradually changes into rhombic sulphur.
- iii. It has rubber like transparent yellow threads and is insoluble in CS<sub>2</sub> and H<sub>2</sub>O.
- iv. Its specific gravity is 1.95 g cm<sup>-3</sup>. Plastic sulphur is regarded as a super-cooled liquid, i.e., a liquid which because of rapid cooling below its melting point has no time to settle in a crystalline form.

#### Structure:

Plastic sulphur consists of zig-zag chains (Figure 3.10) and sometimes S<sub>8</sub> and other rings.

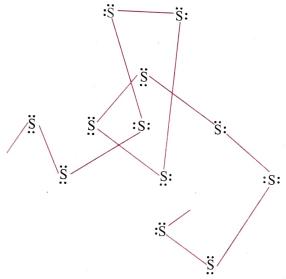


Fig. 3.10 Zig-zag chains of sulphur atoms in plastic sulphur

- 3. Unstable small molecules  $S_n$  (n = 2-5): These molecules exist in different concentrations in liquid sulphur at higher temperatures and in sulphur vapours. S2 species predominate at about 1000 K. Like dioxygen (O2), S2 is paramagnetic and blue coloured and presumably has similar bonding.
- 4. Preparation of milk of sulphur:

It is obtained by boiling milk of lime with sulphur and decomposing the calcium pentasulphide thus formed with HCl, when milk of sulphur is precipitated as white amorphous precipitate.

$$3Ca(OH)_2 + 12S \longrightarrow 2CaS_5 + CaS_2O_3 + 3H_2O$$
  
Milk of lime

$$3CaS5 + CaS2O3 + 6HCl \longrightarrow 3CaCl2 + 3H2O + 12S$$

Properties: Milk of sulphur is soluble in CS<sub>2</sub> and is largely used in medicine.

# 5. Preparation of colloidal of $\delta$ -sulphur:

Sulphur is precipitated in the colloidal form when hydrogen

sulphide is bubbled through nitric acid or when  $Na_2S_2O_3$ solution is treated with dil. HCl.

i. 
$$2HNO_3 \longrightarrow 2NO_2 + H_2O + [O]$$
  
 $H_2S + [O] \longrightarrow S + H_2O$ 

$$2HNO_3 + H_2S \longrightarrow S + 2NO_2 + 2H_2O$$
Colloidal

#### Ionic equation:

$$2H^{\oplus} + e^{\ominus} + NO_3^{\ominus} \longrightarrow NO_2 + H_2O] \times 2$$
  
S<sup>2-</sup> \longrightarrow S + 2e<sup>\Omega</sup>

$$S^{2-} \longrightarrow S + 2e^{\Theta}$$

$$2NO_3^{\Theta} + 4H^{\oplus} + S^{2-} \longrightarrow S + 2NO_2 + 2H_2O$$
ii.  $Na_2S_2O_3 + 2HCI \longrightarrow 2NaCI + SO_2 + S + H_2O$ 

Property: On heating or long steading a self-city to the standard of the self-city of of the sel

ii. 
$$Na_2S_2O_3 + 2HCI \longrightarrow 2NaCI + SO_2 + S + H_2O$$

Property: On heating or long standing, colloidal sulphur changes into the ordinary form.

# 3.11 SULPHUR DIOXIDE (SO<sub>2</sub>)

#### **Preparation:**

- 1. By burning sulphur in air or oxygen  $S + O_2 \xrightarrow{\Delta} SO_2$
- 2. In laboratory, SO<sub>2</sub> can be prepared by
  - a. Heating sulphur with conc. H<sub>2</sub>SO<sub>4</sub>  $S + 2H_2SO_4 \xrightarrow{\Delta} 2H_2O + 3SO_2$
  - **b.** Heating Cu turnings with conc. H<sub>2</sub>SO<sub>4</sub>  $Cu + 2H_2SO_4 \xrightarrow{\Delta} CuSO_4 + SO_2 + 2H_2O_4$
  - c. Treating a sulphite with dil. H<sub>2</sub>SO<sub>4</sub>  $Na_2SO_3 + H_2SO_4 \longrightarrow SO_2 + Na_2SO_4 + H_2O_4$  $SO_3^{2-} + 2H^{\oplus} \longrightarrow SO_2^{\uparrow} + H_2O$

The gas dried, liquefied under pressure and stored in steel cylinders.

3. In industry, SO<sub>2</sub> is prepared by roasting of sulphides.

$$2ZnS + 3O_2 \longrightarrow 2ZnO + 2SO_2$$

$$4FeS_2 + 11O_2 \longrightarrow 2Fe_2O_3 + 8SO_2$$

4. In places, where gypsum or anhydrite ore is found in abundance, SO2, can be obtained on a large scale by heating gypsum or anhydrite with carbon at ~ 1000°C

$$2CaSO_4 + C \longrightarrow 2CaO + 2SO_2 + CO_2$$

# **Properties:**

# Physical properties:

- 1. It is heavier than air.
- 2. It is highly soluble in water.
- 3. It can be easily liquefied to a colourless liquid at -10°C and into a snowlike solid at -76°C.
- 4. It is a colourless gas with a pungent, suffocating odour.

### Chemical properties:

1. Acidic nature: Sulphur dioxide dissolves in water to form sulphurous acid, and thus acts as an acidic oxide.

$$SO_{2(g)} + H_2O_{(l)} \longrightarrow H_2SO_{3(aq)}$$

Therefore, SO<sub>2</sub> is regarded as anhydride of sulphurous acid. Its aqueous solution is acidic and turns blue litmus red. SO<sub>2</sub>, being acidic undergoes the following reactions:

**a.** It reacts readily with sodium hydroxide solution, forming sodium sulphite, which then reacts with more sulphur dioxide to form sodium bisulphite (sodium hydrogen sulphite).

$$\begin{split} 2\text{NaOH}_{(\text{aq})} + \text{SO}_{2(\text{g})} & \longrightarrow \text{Na}_2\text{SO}_{3(\text{aq})} + \text{H}_2\text{O}_{(\text{I})} \\ & \text{Sodium sulphite} \\ \text{Na}_2\text{SO}_{3(\text{aq})} + \text{SO}_{2(\text{g})} + \text{H}_2\text{O}_{(\text{I})} & \longrightarrow 2\text{NaHSO}_{3(\text{aq})} \\ & \text{Sodium bisulphite} \end{split}$$

 It also decomposes carbonates and bicarbonates evolving CO<sub>2</sub> gas.

$$\begin{aligned} &\text{NaHCO}_3 + \text{SO}_2 \longrightarrow \text{NaHSO}_3 + \text{CO}_2 \\ &2\text{SO}_2 + \text{Na}_2\text{CO}_3 + \text{H}_2\text{O} \longrightarrow 2\text{NaHSO}_3 + \text{CO}_2 \\ &2\text{NaHSO}_3 + \text{Na}_2\text{CO}_3 \longrightarrow 2\text{Na}_2\text{S}_2\text{O}_{3\text{(hypo)}} \end{aligned}$$

c. Action on lime water: Like CO<sub>2</sub>, it turns lime water milky due to the formation of insoluble calcium sulphite. However, if SO<sub>2</sub> is passed for a long time, milkiness disappears due to the formation of soluble sodium bisulphite.

$$\begin{aligned} \text{Ca(OH)}_2 + \text{SO}_2 &\longrightarrow \text{CaSO}_3 + \text{H}_2\text{O} \\ & \text{(Milkiness)} \end{aligned}$$

$$\begin{aligned} \text{CaSO}_3 + \text{SO}_2 + \text{H}_2\text{O} &\longrightarrow \text{Ca(HSO}_3)_2 + \text{H}_2\text{O} \\ & \text{Calcium bisulphite (soluble)} \end{aligned}$$

2. Non-supporter of combustion: SO<sub>2</sub> gas is neither combustible nor a supporter of combustion. However, certain substances like heated carbon, lighted magnesium ribbon or heated potassium metal continue to burn on heating.

$$C + SO_2 \longrightarrow CO_2 + S$$

$$2Mg + SO_2 \longrightarrow 2 MgO + S$$

$$4K + 3SO_2 \longrightarrow K_2SO_3 + K_2S_2O_3$$

This is due to the reason that high heat of the reaction dissociates  $SO_2$  to S and  $O_2$  and the  $O_2$  thus produced helps combustion.

3. Reducing nature: In presence of moisture, SO<sub>2</sub> acts as a good reducing agent. Its reducing character is due to the evolution of nascent hydrogen.

$$SO_2 + 2H_2O \longrightarrow H_2SO_4 + 2[H]$$

#### Ionic equation:

$$SO_2 + 2H_2O \longrightarrow SO_4^{2-} + 4H^{\oplus} + 2e^{\ominus}$$

Few examples are as follows:

**a.** Reduces halogens to halogen acids  $(X_2 \longrightarrow X^{\odot})$ 

$$SO_2 + 2H_2O \longrightarrow SO_4^{2-} + 4H^{\oplus} + 2e^{\Theta}$$
  
 $Cl_2 + 2e^{\Theta} \longrightarrow 2Cl^{\Theta}$ 

$$SO_2 + 2H_2O + Cl_2 \longrightarrow SO_4^{2-} + 4H^{\oplus} + 2Cl^{\Theta}$$

**b.** It decolourises pink violet colour of acidified KMnO<sub>4</sub> solution, as SO<sub>2</sub> reduces MnO<sub>4</sub>  $^{\odot}$  to Mn<sup>2+</sup>

Ionic equation:

$$[MnO_{4}^{\Theta} + 8H^{\oplus} + 5e^{\Theta} \longrightarrow Mn^{2+} + 4H_{2}O] \times 2$$

$$[SO_{2} + 2H_{2}O \longrightarrow SO_{4}^{2-} + 4H^{\oplus} + 2e^{\Theta}] \times 5$$

$$2MnO_{4}^{\Theta} + 5SO_{2} + 2H_{2}O \longrightarrow 2Mn^{2+} + 4H^{\oplus} + 5SO_{2}^{2-}$$

c. It turns orange coloured potassium dichromate solution green ( $Cr_2O_7^{2-} \longrightarrow Cr^{3+}$ )  $Cr_2O_7^{2-} + 14H^{\oplus} + 6e^{\Theta} \longrightarrow 2Cr^{3+} + 7H_2O$   $[SO_2 + 2H_2O \longrightarrow SO_4^{2-} + 4H^{\oplus} + 2e^{\Theta}] \times 3$   $Cr_2O_7^{2-} + 2H^{\oplus} + 3SO_2 \longrightarrow 2Cr^{3+} + H_2O + 3SO_2^{2-}$ 

**d.** It reduces lead dioxide to lead sulphate  $PbO_2 + SO_2 \longrightarrow PbSO_4 (SO_2 \longrightarrow SO_4^{2-} + 2e^{O_1})$ 

e. It reduces acidified potassium iodate to iodine

$$(2IO_3^{\ominus} \longrightarrow I_2 + 10e^{\ominus})$$

$$SO_2 + 2H_2O \longrightarrow SO_4^{2-} + 4H^{\oplus} + 2e^{\ominus}] \times 5$$

$$10e^{\ominus} + 2IO_3^{\ominus} + 12H^{\oplus} \longrightarrow I_2 + 6H_2O$$

$$5SO_2 + 2IO_3^{\ominus} + 4H_2O \longrightarrow 5SO_4^{2-} + I_2 + 8H^{\oplus}$$

f. It reduces ferric to ferrous salts  $SO_2 + 2H_2O \longrightarrow SO_4^{2-} + 4H^{\oplus} + 2e^{\ominus}$  $Fe^{3+} + e^{\ominus} \longrightarrow Fe^{2+}] \times 2$ 

$$SO_2 + 2H_2O + 2Fe^{3+} \longrightarrow SO_4^{2-} + 4H^{\oplus} + 2Fe^{2+}$$

Thermal decomposition: SO<sub>2</sub> decomposes at 1200°C producing sulphur trioxide, SO<sub>3</sub> and sulphur.

$$3SO_2 + 2H_2O \xrightarrow{1200^{\circ}C} 2SO_3 + S$$

5. Bleaching action: SO<sub>2</sub> is a mild bleaching agent. Its bleaching action is due to reduction of the vegetable colouring matter by nascent hydrogen liberated in the presence of moisture.

$$SO_2 + 2H_2O \longrightarrow H_2SO_4 + 2[H]$$

Vegetable colouring matter + [H]  $\longrightarrow$  colourless vegetable

Bleaching by SO<sub>2</sub> is, however, **temporary**. When the bleached article is exposed to air, it regains its colour due to oxidation.

Oxidising nature: It acts as a mild oxidising agents
particularly when it reacts with strong reducing agents.

a. Oxidises  $H_2S$  to  $S: 2H_2S + SO_2 \longrightarrow 2H_2O + 3S$ 

b. Active metals are oxidised:

$$3Mg + SO_2 \longrightarrow 2MgO + MgS$$
  
 $4K + 3SO_2 \longrightarrow K_2SO_3 + K_2S_2O_3$   
 $3Fe + SO_2 \longrightarrow 2FeO + FeS$ 

**c.** CO is oxidised to CO<sub>2</sub>:

$$2CO + SO_2 \longrightarrow 2CO_2 + S$$

d. At 1000°C, oxidises hydrogen into water  $2H_2 + SO_2 \xrightarrow{1000^{\circ}C} 2H_2O + S$ 

e. In presence of excess of HCl, stannous and mercurous salts are oxidised

$$2\operatorname{SnCl}_2 + \operatorname{SO}_2 + 4\operatorname{HCl} \longrightarrow 2\operatorname{SnCl}_4 + 2\operatorname{H}_2\operatorname{O} + \operatorname{S}$$

$$2\operatorname{Hg}_3\operatorname{Cl}_2 + \operatorname{SO}_2 + 4\operatorname{HCl} \longrightarrow 4\operatorname{HgCl}_2 + 2\operatorname{H}_2\operatorname{O} + \operatorname{S}$$

# 7. Addition reactions:

a. It combines with O<sub>2</sub> in presence of platinised asbestos at 723 K or in presence of V<sub>2</sub>O<sub>5</sub> at 773 K to form sulphur trioxide

$$SO_2 + O_2 \longrightarrow 2SO_3$$

b. It reacts with Cl<sub>2</sub> in presence of charcoal as catalyst to form sulphuryl chloride

$$SO_2 + Cl_2 \xrightarrow{Charcoal} SO_2Cl_2$$
Sulphuryl chloride

c. It combines with sodium peroxide to form sodium sulphate, Na<sub>2</sub>SO<sub>4</sub>.

$$Na_2O_2 + SO_2 \longrightarrow Na_2SO_4$$

8. With PCl<sub>5</sub>, it gives thionyl chloride, SOCl<sub>2</sub>.

$$PCl_5 + SO_7 \longrightarrow SOCl_2 + POCl_3$$

### Uses:

- 1. In the refining of petroleum and bleaching of sugarcane juice.
- As a bleaching agent for delicate articles like wool, silk and straw.
- 3. In the manufacture of sulphuric acid, calcium hydrogen sulphite and sodium metabisulphite which is used as a preservative for jams, jellies and squashes.
- 4. As a disinfectant for killing germs, fungi and certain moulds.
- 5. As a solvent to dissolve a number of organic and inorganic chemicals.
- 6. As an antichlor for removing excess of Cl<sub>2</sub> from a fabric after bleaching.
- 7. Liquid SO<sub>2</sub> is used as a refrigerant.

# 3.12 SULPHUR TRIOXIDE (SO<sub>3</sub>)

#### Preparation:

1. By dehydrating sulphuric acid with excess of phosphorus pentoxide.

$$6H_2SO_4 + P_4O_{10} \longrightarrow 4H_3PO_4 + 6SO_3$$

2. By heating ferric sulphate strongly.

$$Fe_2(SO_4)_3 \longrightarrow Fe_2O_3 + 3SO_3$$

3. By oxidation of SO<sub>2</sub> with oxygen in presence of a catalyst (commercial method).

$$2SO_2 + O_2 \stackrel{Pt}{\rightleftharpoons} 2SO_3$$

Both  $SO_2$  and  $O_2$  should be completely dry. The mixture is passed over platinised asbestos at 400°C, when  $SO_3$  is formed.

# **Properties:**

- 1.  $SO_3$  exists in three allotropic forms:
  - a. α-SO<sub>3</sub>: It is a chemically active form. It forms long transparent ice like crystals. The melting point of this form is 17°C.

- **b.**  $\beta$ -SO<sub>3</sub>: It is a dimeric form (S<sub>2</sub>O<sub>6</sub>). It forms needle-like silky white crystals. It melts at 32.5°C. Above 50°C, it changes to  $\alpha$ -form.
- c.  $\gamma$ -SO<sub>3</sub>: It is like  $\beta$ -form and obtained by completely drying  $\beta$ -SO<sub>3</sub>. It melts at 62.2°C under 2 atmospheric pressure.
- 2. It dissolves in concentrated sulphuric acid forming oleum (fuming sulphuric acid).

$$H_2SO_4 + SO_3 \longrightarrow H_2S_2O_7$$

3. It dissociates on heating at  $1000^{\circ}$ C into  $SO_2$  and  $O_2$ .

$$2SO_3 \xrightarrow{1000^{\circ}C} 2SO_2 + O_2$$

4. It combines with concentrated hydrochloric acid and forms chloro-sulphonic acid, a derivative of sulphuric acid.

$$SO_3 + HC1 \longrightarrow SO_2 \cdot (OH)C1$$
Chloro-sulphonic acid

5. SO<sub>3</sub> is an acidic oxide. It dissolves in water forming sulphuric acid with evolution of heat.

$$SO_3 + H_2O \longrightarrow H_2SO_4 + heat$$

It reacts with basic oxides forming sulphates.

$$CaO + SO_3 \longrightarrow CaSO_4$$

$$Na_2O + SO_3 \longrightarrow Na_2SO_4$$

**6.** SO<sub>3</sub> acts as an oxidising agent.

Examples:

$$2SO_3 + S \xrightarrow{100^{\circ}C} 3SO_2$$

$$SO_3 + PCl_5 \longrightarrow POCl_3 + SO_2 + Cl_2$$
Phosphoryl chloride

$$SO_3 + 2HBr \longrightarrow H_2O + Br_2 + SO_2$$

#### Uses:

- 1. In the manufacture of sulphuric acid and oleum.
- 2. It is used as a drying agent for gases.

### ILLUSTRATION 3.3

- a. Which form of sulphur shows paramagnetic behaviour?
- **b.** Compounds of fluorine and oxygen are called fluorides and not oxides. Explain.
- **c.** Sulphur disappears when boiled with an aqueous solution of sodium sulphite. Why?

#### Sol.

- a. In vapour state, sulphur partly exists as  $S_2$  molecules and  $S_2$  molecule like  $O_2$  molecule has two unpaired electrons in the antibonding  $\pi^*$ -orbitals and exhibits paramagnetic nature.
- b. This is because of higher electronegativity of fluorine than oxygen. In naming a compound, the electropositive or less electronegative element is taken first, thus, the compounds of fluorine and oxygen are called oxygen fluorides and fluorine oxides.
- c. Sulphur combines with sodium sulphite and forms sodium thiosulphate which is soluble in water and hence S disappears.

# ILLUSTRATION 3.4

Knowing the electron gain enthalpy values for  $O \longrightarrow O^{\Theta}$  and  $O \longrightarrow O^{2-}$  as  $-141 \text{ kJ mol}^{-1}$  and  $+702 \text{ kJ mol}^{-1}$  respectively, how can you account for the formation of a large number of oxides having  $O^{2-}$  species and not  $O^{\Theta}$ ?

**Sol.** Although the formation of  $O^{2-}$  anion requires more energy in comparison to the formation of  $O^{\odot}$  anion (actually energy is released), yet in large number of oxides, oxygen is divalent in nature. This is due to the fact that lattice energies of the oxides having  $O^{2-}$  anions are very high on account of greater magnitude of electrostatic forces of attraction.

# 3.13 OXOACIDS OF SULPHUR

A large number of oxyacids are known in the case of sulphur either in free state or in the form of salts or both. Oxyacids with S–S links are called thioacids. Acids having sulphur in lower oxidation state belong to -ous series while those having sulphur in higher oxidation state belong to -ic series. The name, formula, structure, O.S. and properties of some oxo-acids of sulphur are given in Table 3.2.

# 3.14 SULPHURIC ACID (H<sub>2</sub>SO<sub>4</sub>)

Sulphuric acid, in ancient days, was called **oil of vitriol** as it was prepared by distilling ferrous sulphate,  $FeSO_4 \cdot 7H_2O$  (also known as **green vitriol**).

FeSO<sub>4</sub>·7H<sub>2</sub>O 
$$\xrightarrow{\text{Distil}}$$
 Fe<sub>2</sub>O<sub>3</sub> + H<sub>2</sub>SO<sub>4</sub> + SO<sub>2</sub> + 13H<sub>2</sub>O  
Sulphuric acid is considered as **king of chemicals**. The prosperity of any country is measured by the amount of H SO<sub>2</sub> it consumes

of any country is measured by the amount of  $H_2SO_4$  it consumes.  $H_2SO_4$  is a chemical of great commercial importance as it is used practically in every important industry.

# 3.14.1 MANUFACTURE OF H<sub>2</sub>SO<sub>4</sub> BY CONTACT PROCESS

Sulphuric acid is manufactured these days by contact process (Figure 3.11) which involves the following steps:

Table 3.2 Some Oxyacid of sulphur

1. Production of SO<sub>2</sub> by burning sulphur or sulphide ores, e.g.

$$S_8 + 8O_2 \xrightarrow{\Delta} 8SO_2$$
;  $4FeS_2 + 11O_2 \xrightarrow{\Delta} 2Fe_2O_3 + 8SO_3$   
(Air) Iron pyrites

2. Catalytic oxidation of sulphur dioxide by air to give sulphur trioxide.

$$2SO_{2(g)} + O_{2(g)} \rightleftharpoons 2SO_{3(g)}; \quad \Delta_f H^{\odot} = -196.6 \text{ kJ mol}^{-1}$$

This step is the key step in the manufacture of H<sub>2</sub>SO<sub>4</sub>. In accordance with Le Chatelier's principle, the favourable conditions for the maximum yield of SO<sub>3</sub> are as follows:

- a. High pressure: Since the forward reaction proceeds with decrease in number of moles, hence high pressure will favour the reaction. In actual practice, a pressure of about 2 bars is used. This is because gases are acidic and corrosion of the plant occurs at high pressures.
- b. Low temperature: Since the forward reaction is exothermic, therefore, low temperature will favour the reaction. However, rate of the reaction decreases with decrease in temperature. Therefore, the reaction is carried out at an optimum temperature of 720 K.
- c. Use of a catalyst: To increase the rate of reaction at low temperature, a catalyst e.g.  $V_2O_5$  or  $Fe_2O_3$  is used. Since platinum is costly and is easily poisoned by arsenic impurities usually present in  $SO_2$ , therefore, these days, divanadium pentoxide  $V_2O_5$  is used because it is cheaper as well as not easily poisoned.
- **d. Purity of gases:** To prevent poisoning of catalyst, the gases must be free from the impurities of As<sub>2</sub>O<sub>3</sub> dust particles and moisture.
- e. Excess of oxygen: To have maximum yield of SO<sub>3</sub>, O<sub>2</sub> is used in excess.
- f. Absorption of sulphur trioxide in 98% sulphuric acid to form oleum.

$$SO_3 + H_2SO_4 \longrightarrow H_2S_2O_7$$
 (oleum)

Name of acid	Formula	O.S.	Structure	
Sulphurous acid series:			Structure	Property
a. Sulphurous acid	H <sub>2</sub> SO <sub>3</sub>	+4	$(S \leftarrow sp^3)$	Acts as oxidising and reducing agent
			HO NO S	
b. Thiosulphurous acid	$H_2S_2O_2$	+1	HO————————————————————————————————————	-
. Hyposulphurous acid or Hydrosulphurous acid	$H_2S_2O_4$	+3	HO $-\overset{\circ}{\overset{\circ}{\overset{\circ}{\Box}}}\overset{\circ}{\overset{\circ}{\overset{\circ}{\Box}}}$ HO $-\overset{\circ}{\overset{\circ}{\overset{\circ}{\Box}}}\overset{\circ}{\overset{\circ}{\overset{\circ}{\Box}}}$	
or Dithionous acid  Di or pyrosulphurous acid	$H_2S_2O_5$	+4	HO $S$	-S-S-linkage, not known in fi

1			p-Block	Group 16 Elements: The Oxygen Family 3.2
Sulphuric acid series:				
e. Sulphuric acid	H <sub>2</sub> SO <sub>4</sub>	+6	$\bigcup_{\substack{\text{S} \\ \text{S} = 0}} sp^3$	Acts as dehydrating, oxidising and pickling agent
f. Thiosulphuric acid	H <sub>2</sub> S <sub>2</sub> O <sub>3</sub>	+6	HO OH  S S S O OH  OH	_
g. Pyrosulphuric acid	H <sub>2</sub> S <sub>2</sub> O <sub>7</sub>	+6	$sp^3$ OH $sp^3$ $S$	It is known as fuming sulphuric acid or anhydride of sulphuric acid or oleum
Thionic acid series:			O	
h. Dithionic acid	$H_2S_2O_6$	+5	HO-S $S$ $S$ $O$ $O$ $S$ $O$ $O$ $S$ $O$ $O$ $S$ $O$ $O$ $O$ $S$ $O$ $O$ $S$ $O$	- · ·
i. Polythionic acid	$H_2S_nO_6$	+5		-
	(n=1  to  6)		$HO-\ddot{S}$ $(S)_n$ $\ddot{S}$ $OOH$ $Sp^3$ $OOH$	
Peroxy acid series:				
j, Peroxy monosulphuric acid (Caro's acid)	H <sub>2</sub> SO <sub>5</sub>	+6	НО—  ÖÖ_—   ^	-O-O-linkage
			$ \stackrel{\text{\tiny II}}{\circ} \phantom{\phantom{\phantom{\phantom{\phantom{\phantom{\phantom{\phantom{\phantom{\phantom{\phantom{\phantom{\phantom{\phantom{\phantom{\phantom{\phantom{\phantom{\phantom$	
c. Peroxy disulphuric acid (Marshall's acid)	$H_2S_2O_8$	+6	HO— $\stackrel{\circ}{=}$ $\stackrel$	-O-O-linkage
Sulphoxylic acid	H <sub>2</sub> SO <sub>2</sub>	+2	Not known	Not known in free state
-	2 Z		I VOL KIIOWII	INOU KHOWII III IFEE STATE

g. Dilution of oleum to get sulphuric acid of desired concentration.

$$H_2S_2O_7 + H_2O \longrightarrow 2H_2SO_4$$

3. Absorption of SO<sub>3</sub> in H<sub>2</sub>SO<sub>4</sub> to give oleum (H<sub>2</sub>S<sub>2</sub>O<sub>7</sub>).

In industry, the two steps, i.e., absorption of SO<sub>3</sub> in H<sub>2</sub>SO<sub>4</sub> to form oleum and its subsequent dilution with water are carried out simultaneously to make the process a continuous one and also to reduce the cost.

The sulphuric acid obtained by the contact process is 96–98% pure.

The plant consists of the following parts:

- 1. Pyrite or sulphur burners: Sulphur dioxide is produced by roasting pyrites or by burning sulphur in air.
- 2. Purifying unit: It consists of the following parts:
  - **a. Dust remover:** Dust is removed either by blowing steam or by using Cottrell electrical precipitator.
  - **b.** Scrubber or washer: Soluble impurities are removed by washing gases with water.

- c. Drier: A spray of conc. H<sub>2</sub>SO<sub>4</sub> is used for drying of gases.
- **d. Arsenic purifier:** Gelatinous Fe(OH)<sub>3</sub> is used to absorb impurities.
- 3. Catalytic converter: The pure gases coming from the testing box are preheated to 720 K in a preheater. The gases are then passed over a catalyst consisting either of platinised asbestos or V<sub>2</sub>O<sub>5</sub>. Under these conditions, SO<sub>2</sub> gets oxidised to SO<sub>3</sub> and the heat produced in the reaction is used for heating the gases in the preheater.
- **4. Absorption tower:** SO<sub>3</sub> from the catalytic converter is introduced at the base of the absorption tower from the top of which H<sub>2</sub>SO<sub>4</sub> (98%) is showered. As SO<sub>3</sub> moves above, it is absorbed by H<sub>2</sub>SO<sub>4</sub> forming oleum.

Oleum is then diluted with water to get H<sub>2</sub>SO<sub>4</sub> of desired concentration.

It may be noted that sulphur trioxide is not directly absorbed in water to form sulphuric acid because it forms a dense fog of sulphuric acid which does not condense easily.

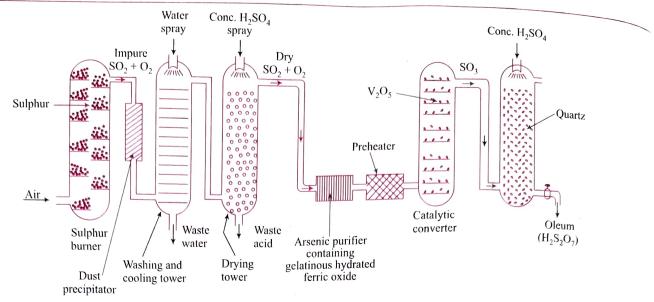


Fig. 3.11 Contact process for the manufacture of sulphuric acid

#### 3.14.2 STRUCTURES

Both sulphuric acid and sulphate ion have tetrahedral structure in which sulphur is  $sp^3$ -hybridised.

In sulphate ion, all the S–O bond lengths are equal, i.e. 149 pm. hence, it is a resonance hybrid of four structures (I, II, III and IV) as shown in Figure 3.12.

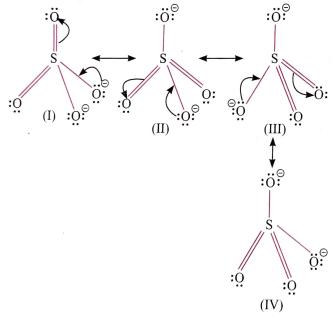


Fig. 3.12 Resonance of structure of SO<sub>2</sub><sup>2-</sup> ion

#### 3.14.3 PROPERTIES

#### Physical properties:

- Pure concentrated sulphuric acid is a colourless syrupy liquid.
- 2. Concentrated sulphuric acid (98.3%) has a specific gravity of 1.84 at 298 K. It boils at 590 K and freezes into colourless crystals at 283 K.
- 3. It forms azeotrope, i.e., constant boiling mixture containing  $98.3\% \text{ H}_2\text{SO}_4$  and 1.7% water.
- **4.** It is highly corrosive and produces burns on the skin (due to dehydration of skin).

5. Sulphuric acid has a high boiling point (590 K) and a high viscosity because its molecules are associated due to intermolecular hydrogen bonding as shown in Figure 3.13.

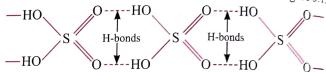


Fig. 3.13 Intermolecular H-bonding in H<sub>2</sub>SO<sub>2</sub>

6. H<sub>2</sub>SO<sub>4</sub> has a strong affinity for water various hydrates such as H<sub>2</sub>SO<sub>4</sub>·H<sub>2</sub>O, H<sub>2</sub>SO<sub>4</sub>·2H<sub>2</sub>O, H<sub>2</sub>SO<sub>4</sub>·3H<sub>2</sub>O and H<sub>2</sub>SO<sub>4</sub>·4H<sub>2</sub>O are known. When sulphuric acid dissolves in water, a large amount of heat is produced which may spurt the acid out of the container. Hence, care must be taken while preparing dilute sulphuric acid from concentrated sulphuric acid (spurting of acid). Therefore conc. H<sub>2</sub>SO<sub>4</sub> is always diluted by adding the acid slowly into water with constant stirring and not by adding water to acid.

#### **Chemical properties:**

- **1. Dissociation:** At 444°C (or 717 K), the vapours of H<sub>2</sub>SO<sub>4</sub> dissociate into SO<sub>3</sub> and steam (H<sub>2</sub>O).
- 2. Acidic character: In aqueous solution, H<sub>2</sub>SO<sub>4</sub> ionises in two steps:

$$H_2SO_{4(aq)} \longrightarrow H^{\oplus}_{(aq)} + HSO_{4(aq)}^{\ominus}; \quad K_{a_1} = 1 \times 10^3$$
 $HSO_{4(aq)}^{\ominus} \longrightarrow H^{\oplus}_{(aq)} + SO_{4(aq)}^{2-}; \quad K_{a_2} = 1.2 \times 10^{-2}$ 
The larger value of  $K_{a_1} (K_{a_1} > 10)$  means that  $H_2SO_4$  is largely dissociated into  $H^{\oplus}$  and  $HSO_4^{\ominus}$ . Greater the value of dissociation constant  $(K_a)$ , stronger is the acid.

Thus,  $H_2SO_4$  acts as a strong dibasic acid and forms two series of salts – normal sulphates such as sodium sulphates  $(Na_2SO_4)$  and acid sulphates or hydrogen sulphates of

a. It reacts with electropositive metals to evolved  $H_{2(g)}$  $Zn + H_2SO_4 \longrightarrow ZnSO_4 + H_{2(g)}$ 

bisulphates such as sodium bisulphate (NaHSO<sub>4</sub>).

$$Fe + H_2SO_4 \longrightarrow FeSO_4 + H_{2(g)}$$

It displaces more volatile acids from their metal salts.

$$2\text{NaCl} + \text{H}_2\text{SO}_4 \longrightarrow \text{Na}_2\text{SO}_4 + 2\text{HCl}$$

$$Ca_3(PO_4)_2 + 3H_2SO_4 \longrightarrow 3CaSO_4 + 2H_3PO_4$$

$$CaC_2O_4 + H_2SO_4 \longrightarrow CaSO_4 + H_2C_2O_4$$

$$FeS + H_2SO_4 \longrightarrow FeSO_4 + H_2S$$

$$2CH_3COONa + H_2SO_4 \longrightarrow Na_2SO_4 + 2CH_3COOH$$

$$2\text{NaNO}_3 + \text{H}_2\text{SO}_4 \longrightarrow \text{Na}_2\text{SO}_4 + 2\text{HNO}_3$$

$$CaF_2 + H_2SO_4 \longrightarrow CaSO_4 + 2HF$$

It forms two series of salts with bases.

$$NaOH + H_2SO_4 \longrightarrow NaHSO_4 + H_2O;$$

$$2\text{NaOH} + \text{H}_2\text{SO}_4 \longrightarrow \text{Na}_2\text{SO}_4 + 2\text{H}_2\text{O}$$
Sodium

It decomposes carbonates and bicarbonates into carbon dioxide.

$$Na_2CO_3 + H_2SO_4 \longrightarrow Na_2SO_4 + H_2O + CO_2$$
  
 $NaHCO_3 + H_2SO_4 \longrightarrow NaHSO_4 + H_2O + CO_2$ 

- 3. Dehydrating agent: As conc. H<sub>2</sub>SO<sub>4</sub> has a strong affinity for water, it acts as a strong dehydrating agent. For example:
  - a. It removes water of crystallisation from hydrated salts. For example,

CuSO<sub>4</sub>·5H<sub>2</sub>O

Hydrated copper sulphate (blue)

Conc. 
$$H_2SO_4$$

CuSO<sub>4</sub> + 5H<sub>2</sub>O

Anhydrous copper sulphate

b. Charring of sugar

Chairing of sagar

$$C_{12}H_{22}O_{11}$$

Conc.  $H_2SO_4$ 

Sugar charcoal

Sugar charcoal

c. Dehydration of formic acid and oxalic acid

$$\text{HCOOH} \xrightarrow{\text{Conc. H}_2\text{SO}_4} \text{H}_2\text{O} + \text{CO}$$

Formic acid

COOH COOH 
$$Conc. H_2SO_4 \rightarrow H_2O + CO + CO_2$$

Oxalic acid

d. Action on ethyl alcoh

i. 
$$CH_3CH_2OH \xrightarrow{Conc. H_2SO_4} CH_2 = CH_2 + H_2O$$
  
Ethyl alcohol Ethylene

(Intramolecular dehydration)

ii. 
$$2CH_3CH_2OH \xrightarrow{Conc. H_2SO_4} CH_3CH_2OCH_2CH_3 + H_2O$$
Ethyl alcohol

Diethyl ether

(Intermolecular dehydration)

Drying of gases: Many gases such as O2, N2, Cl2, HCl, etc. which do not react with conc.  $H_2\tilde{SO}_4$  can be dried by passing them through a bubbler containing conc. H<sub>2</sub>SO<sub>4</sub>.

Cloth, wood, paper etc. are all charred in concentrated  $H_2SO_4$ .

4. Oxidising agent: Hot concentrated sulphuric acid is a moderately strong oxidising agent since it on decomposition gives nascent oxygen, oxidising power of H<sub>2</sub>SO<sub>4</sub> is intermediate between H<sub>3</sub>PO<sub>4</sub> and HNO<sub>3</sub>.

$$H_2SO_4 \longrightarrow H_2O + SO_2 + [O]$$
(Hot conc.)

or 
$$SO_4^{2-} + 4H^{\oplus} + 2e^{\ominus} \longrightarrow SO_2 + 2H_2O$$

a. It oxidises sulphur to sulphur dioxide

$$[SO_4^{2-} + 4H^{\oplus} + 2e^{\ominus} \longrightarrow SO_2 + 2H_2O] \times 2$$
  
S + 2H<sub>2</sub>O \rightarrow SO<sub>2</sub> + 4H^{\theta} + 2e^{\ightarrow}

$$2SO_4^{2-} + 4H^{\oplus} + S \longrightarrow 3SO_2 + 2H_2O$$
**b.** It oxidises carbon to carbon dioxide

$$[SO_4^{2-} + 4H^{\oplus} + 2e^{\Theta} \longrightarrow SO_2 + 2H_2O] \times 2$$
  
C + 2H<sub>2</sub>O \rightarrow CO<sub>2</sub> + 4H^{\theta} + 4e^{\theta}

$$2SO_4^{2-} + 4H^{\oplus} + C \longrightarrow CO_2 + 2SO_2 + 2H_2O$$

c. It oxidises phosphorous to phosphoric acid or phosphate

$$[SO_4^{2-} + 4H^{\oplus} + 2e^{\Theta} \longrightarrow SO_2 + 2H_2O] \times 10$$
  
 $P_4 + 16H_2O \longrightarrow 4PO_4^{3-} + 32H^{\oplus} + 20e^{\Theta}$ 

$$10SO_4^{2-} + 8H^{\oplus} + P_4 \longrightarrow 10SO_2 + 4H_2O + 4PO_4^{3-}$$

d. It oxidises metals such as Cu, Pb, Hg, Ag first to their oxides and then to their corresponding sulphates liberating SO, gas.

$$SO_4^{2-} + 4H^{\oplus} + 2e^{\ominus} \longrightarrow SO_2 + 2H_2O$$
  
 $Cu \longrightarrow Cu^{2+} + 2e^{\ominus}$ 

$$SO_4^{2-} + 4H^{\oplus} + Cu \longrightarrow SO_2 + 2H_2O + Cu^{2+}$$

e. It oxidises iodide to iodine

$$SO_4^{2-} + 4H^{\oplus} + 2e^{\Theta} \longrightarrow SO_2 + 2H_2O$$
  
 $2I^{\Theta} \longrightarrow I_2 + 2e^{\Theta}$ 

$$SO_4^{2-} + 4H^{\oplus} + 2I^{\ominus} \longrightarrow SO_2 + 2H_2O + I_2$$

Similarly bromide is oxidised to bromine gas.

In the presence of Hg as a catalyst, naphthalene is oxidised to phthalic acid.

$$\begin{array}{c}
& 9H_2SO_4 \\
& + Hg
\end{array}$$
COOH
COOH

Naphthalene

$$+10H_2O + 9SO_2 + 2CO_2$$

- 5. Action on salts: Due to its low volatility conc. H<sub>2</sub>SO<sub>4</sub> can be used to manufacture more volatile acids from their corresponding salts.
  - a. With dilute acid: Bicarbonate, sulphides, carbonates, sulphites, thiosulphates and nitrites are decomposed by dil. H<sub>2</sub>SO<sub>4</sub> at room temperature. For example,

i. 
$$2\text{NaHCO}_3 + \text{H}_2\text{SO}_4 \longrightarrow [2\text{NaHSO}_4 + 2\text{H}_2\text{CO}_3]$$
  
 $\longrightarrow 2\text{NaHSO}_4 + 2\text{CO}_2 + 2\text{H}_2\text{O}_3$ 

ii. 
$$Na_2S + H_2SO_4 \longrightarrow 2Na_2SO_4 + H_2S$$

iii. 
$$Na_2CO_3 + H_2SO_4 \longrightarrow [2Na_2SO_4 + H_2CO_3]$$
  
Strong acid Weak acid
$$\longrightarrow Na_2SO_4 + CO_2 + H_2O$$
iv.  $Na_2SO_3 + H_2SO_4 \longrightarrow [2Na_2SO_4 + 2H_2SO_3]$ 

$$\longrightarrow Na_2SO_4 + SO_2 + H_2O$$
v.  $2NaNO_2 + H_2SO_4 \longrightarrow [Na_2SO_4 + 2HNO_2]$ 

$$\longrightarrow Na_2SO_4 + NO + NO_2 + H_2O$$
vi.  $Na_2S_2O_3 + H_2SO_4 \longrightarrow [Na_2SO_4 + H_2SO_3 + S]$ 

$$\longrightarrow Na_2SO_4 + SO_2 + H_2O + S]$$

b. With hot concentrated acid: Chlorides, fluorides, acetates, nitrates and oxalates are decomposed by hot conc. H,SO<sub>4</sub> liberating their corresponding acids. For example,

i. 
$$NaCl+ H_2SO_4 \longrightarrow NaHSO_4 + HCl$$
  
ii.  $CaF_2 + H_2SO_4 \longrightarrow CaSO_4 + 2HF$ 

iii. 
$$CH_3COOK + H_2SO_4 \longrightarrow K_2SO_4 + 2CH_3COOH$$

iv. 
$$KNO_3 + H_2SO_4 \longrightarrow KHSO_4 + HNO_3$$

v. 
$$| COONa + H_2SO_4 \longrightarrow | COOH + Na_2SO_4$$

6. Precipitation reactions: When an aqueous solution of barium, strontium, calcium and lead salts are treated with dil. H2SO4, white precipitate of their corresponding metal sulphates are formed, which are insoluble in conc. H<sub>2</sub>SO<sub>4</sub> and conc. HNO3.

$$BaCl_{2} + H_{2}SO_{4} \longrightarrow BaSO_{4} + 2HCl$$
White ppt.
$$Ba^{2+} + SO_{4}^{2-} \longrightarrow BaSO_{4} \downarrow + 2HCl \text{ (Test for SO}_{4}^{2-} \text{ ion)}$$
White ppt.
$$CaCl_{2} + H_{2}SO_{4} \longrightarrow CaSO_{4} \downarrow + 2HCl$$
White ppt.
$$(CH_{2}COO)_{4}Ph + H_{2}SO_{4} \longrightarrow PhSO_{4} \downarrow + 2CH_{2}COON_{4}$$

$$(CH_3COO)_2Pb + H_2SO_4 \longrightarrow PbSO_4 \downarrow + 2CH_3COOH$$
White ppt.

### 7. Miscellaneous reactions:

a. Reaction with potassium ferrocyanide: Carbon monoxide (CO) is formed on heating  $K_4[Fe(CN)_6]$  with  $H_2SO_4$ .

$$\begin{array}{c} \text{K}_{4}[\text{Fe}(\text{CN})_{6}] + 6\text{H}_{2}\text{SO}_{4} + 6\text{H}_{2}\text{O} \xrightarrow{\text{Heat}} 2\text{K}_{2}\text{SO}_{4} + \\ \text{Fe}\text{SO}_{4} + 3(\text{NH}_{4})_{2}\text{SO}_{4} + 6\text{CO} \\ \end{array}$$

b. Reaction with sulphur trioxide: SO<sub>3</sub> dissolves in conc. H<sub>2</sub>SO<sub>4</sub> forming oleum or fuming H<sub>2</sub>SO<sub>4</sub>.

$$H_2SO_4 + SO_3 \longrightarrow H_2S_2O_7$$
 (oleum)

c. Reaction with PCI5: Depending upon the amount of  $PCl_5$  used one or both the hydroxyl groups of  $H_2SO_4$ can be replaced by chlorine atoms.

$$\begin{array}{c} O \\ \parallel \\ S \\ O \end{array} O H \stackrel{+ \ 2PCl_5}{(Excess)} \longrightarrow \begin{array}{c} O \\ \parallel \\ Cl \end{array} \stackrel{+ \ 2POCl_3 + H_C}{(Excess)} \\ O \\ Sulphuryl\ chloride \end{array}$$

d. Reaction with KClO<sub>3</sub>: On heating with conc. H<sub>2</sub>S<sub>0</sub> KClO<sub>3</sub> gives chlorine dioxide (ClO<sub>2</sub>) with  $\exp \log_{10}$  $3KCIO_3 + H_2SO_4 \xrightarrow{330 \text{ K}} 3KHSO_4 + HCIO_4 +$ 

e. Reaction with phosphorous pentoxide: H<sub>2</sub>SO<sub>4</sub> reaction with phosphorous pentoxide to lose water and  $f_{0\eta_{lh}}$ 

$$H_2SO_4 + P_2O_5 \longrightarrow 2HPO_3 + SO_3$$

### 3.14.4 USES

- 1. In chemical industry: Sulphuric acid is employed in the manufacture of various chemicals such as hydrochlotic acid, nitric acid, phosphoric acid, sulphates and bisulphates diethyl ether, etc.
- 2. In dyes, drugs, paints, pigments and detergents: It is used directly or indirectly in the manufacture of number of chemicals such as dyes, drugs, paints, pigments and detergents.
- 3. In fertiliser industry: Sulphuric acid is used to manufacture fertilisers like ammonium sulphate and super phosphate of lime.
- 4. In the manufacture of explosives: A mixture of sulphuric acid and nitric acid called nitrating mixture is used for nitration of organic compounds. This nitration process is used for the manufacture of a large number of explosives like dynamite (a mixture of glyceryl trinitrate and glyceryl dinitrate absorbed over Kieselguhr - a porous earth), gun cotton (nitrocellulose) T.N.T. (2,4,6- trinitrotoluene), picno acid (2,4,6-trinitrophenol), etc.
- 5. In petroleum refining: Crude petroleum is treated with sulphuric acid to remove unwanted sulphur and other tarry compounds.
- 6. In metallurgy: A number of metals like copper and silver are extracted from their ores using sulphuric acid.
- 7. In pickling. Sulphuric acid is used for cleaning (pickling) the surface of metals before enamelling, electroplating and galvanising.
- 8. In leather industry for tanning.
- 9. As laboratory reagent: It is widely used in laboratory as a drying and dehydrating agent.
- 10. In lead storage batteries as electrolyte.

# 3.15 COMPOUNDS OF SULPHUR

Sodium thiosulphate (Hypo)  $Na_2S_2O_3 \cdot 5H_2O$ 

### **Preparation:**

1. It is prepared by heating a solution of Na<sub>2</sub>SO<sub>3</sub> with finally powdered sulphur in an alkaline medium until yellow colour due to sulphur disappears.

$$Na_2SO_3 + S \xrightarrow{330 \text{ K}} Na_2S_2O_3$$

2. It can also be prepared by adding requisite amount of I<sub>2</sub> to a mixture of Na<sub>2</sub>S and Na<sub>2</sub>SO<sub>3</sub> (Spring's reaction).

$$\begin{array}{ccc} Na_2S & + & Na_2SO_3 + I_2 \longrightarrow 2NaI + Na_2S_2O_3 \\ & & \text{Sodium sulphite} & \text{Sodium thiosulphate} \end{array}$$

3.  $Pure Na_2S_2O_3$  can be obtained by treating sodium bisulphite with sodium bisulphide followed crystallisation.

$$_{4\text{NaHSO}_{3}} + 2\text{NaHS} \longrightarrow 3\text{Na}_{2}\text{S}_{2}\text{O}_{3} + 3\text{H}_{2}\text{O}$$

4. It was formerly manufactured by boiling  $NaOH_{(aq)}$  with sulphur.

$$_{6}$$
NaOH + 4S  $\longrightarrow$  Na $_{2}$ S $_{2}$ O $_{3}$  + 4Na $_{2}$ S + 3H $_{2}$ O

5. It can also be obtained by passing SO<sub>2</sub> through Na<sub>2</sub>S solution.

$$_{2\mathrm{Na}_{2}\mathrm{S}} + 3\mathrm{SO}_{2} \longrightarrow 2\mathrm{Na}_{2}\mathrm{S}_{2}\mathrm{O}_{3} + \mathrm{S}$$

properties: It is a white crystalline solid soluble in water.

1. With Cl<sub>2</sub> or Br<sub>2</sub>: Cl<sub>2</sub> (or Br<sub>2</sub>) reacts with Na<sub>2</sub>S<sub>2</sub>O<sub>2(aq)</sub> as follows.

$$Cl_2 + H_2O + Na_2S_2O_3 \longrightarrow 2HCl + Na_2SO_4 + S$$

Hypo is thus used as an **antichlor** for removing excess Cl<sub>2</sub> in bleaching industry.

2. With silver salts:

$$2AgNO_3 + Na_2S_2O_3 \longrightarrow Ag_2S_2O_3 + 2NaNO_3$$

$$Ag_2S_2O_3 + H_2O \longrightarrow H_2SO_4 + Ag_2S$$
 (Black)

$$AgBr + 2Na_2S_2O_3 \longrightarrow Na_3[Ag(S_2O_3)_2] + NaBr$$

This reaction has been used in photography to remove undecomposed silver halide on photographic film or paper.

3. With I<sub>2</sub>: This reaction is used in iodometric titrations.

$$2\text{Na}_2\text{S}_2\text{O}_3 + \text{I}_2 \longrightarrow \text{Na}_2\text{S}_4\text{O}_6 + 2\text{NaI}$$

Sodium tetrathionate

 $Na_2S_2O_3$  so produced is colourless, hypo can be used to remove iodine stains from skin and clothes.

# ILLUSTRATION 3.5

What happens when

- i. Concentrated H<sub>2</sub>SO<sub>4</sub> is added to calcium fluoride.
- ii. SO<sub>3</sub> is passed through water?

Sol.

- ii.  $SO_3 + H_2O \longrightarrow H_2SO_4$ Sulphur Water Sulphuric trioxide acid

SO<sub>3</sub> dissolves in water to form H<sub>2</sub>SO<sub>4</sub>.

# ILLUSTRATION 3.6

Give at least one example to explain the following properties

- a. Sulphuric acid is a dibasic acid.
- b. Sulphuric acid is a dehydrating agent.
- c. Sulphuric acid is an oxidising agent.

#### Sol.

a. H<sub>2</sub>SO<sub>4</sub> forms two series of salts, i.e., both the hydrogen atoms are replaceable.

$$H_2SO_4 \rightleftharpoons H^{\oplus} + HSO_4^{\ominus} \rightleftharpoons 2H^{\oplus} + SO_4^{2-}$$
  
 $H_2SO_4 + NaOH \longrightarrow NaHSO_4 + H_2O$ 

Sodium hydrogen sulphate (acid salt)

$$H_2SO_4 + 2NaOH \longrightarrow Na_2SO_4 + 2H_2O$$
Sodium sulphate
(Normal salt)

**b.** H<sub>2</sub>SO<sub>4</sub> has great affinity for water molecules and hence, acts as a dehydrating agent.

$$\text{HCOOH} \xrightarrow{\text{Conc. H}_2\text{SO}_4} \text{H}_2\text{O} + \text{CO}$$

c. H<sub>2</sub>SO<sub>4</sub> oxidises metals, non-metals and other compounds.

$$Cu + 2H_2SO_4(conc.) \longrightarrow CuSO_4 + SO_2 + 2H_2O_4$$

$$S + 2H_2SO_4 \longrightarrow 3SO_2 + 2H_2O$$

$$2HI + H_2SO_4 \longrightarrow I_2 + SO_2 + 2H_2O$$

### ILLUSTRATION 3.7

How will you obtain the following from sulphuric acid?

- a. SO<sub>2</sub>
- **b.**  $SO_3$
- c. SO<sub>2</sub>Cl<sub>2</sub>

#### Sol.

a. SO<sub>2</sub> is obtained by heating copper with conc. H<sub>2</sub>SO<sub>4</sub>.

$$Cu + 2H_2SO_4 \longrightarrow CuSO_4 + SO_2 + 2H_2O_4$$

It can also be obtained by boiling sulphur with conc. H<sub>2</sub>SO<sub>4</sub>.

$$S + 2H_2SO_4 \longrightarrow 3SO_2 + 2H_2O$$

**b.** H<sub>2</sub>SO<sub>4</sub> when titrated with P<sub>2</sub>O<sub>5</sub> loses water and forms SO<sub>3</sub>.

$$H_2SO_4 + P_2O_5 \longrightarrow 2HPO_3 + SO_3$$

**c.** SO<sub>2</sub>Cl<sub>2</sub> is formed when conc. H<sub>2</sub>SO<sub>4</sub> is treated with excess of PCl<sub>5</sub>.

$$H_2SO_4 + 2PCl_5 \longrightarrow SO_2Cl_2 + 2POCl_3 + 2HCl$$

# ILLUSTRATION 3.8

Give reason for the following:

- a. Conc. H<sub>2</sub>SO<sub>4</sub> cannot be used for drying H<sub>2</sub>.
- **b.** KMnO<sub>4</sub> should not be dissolved in conc. H<sub>2</sub>SO<sub>4</sub>.

#### Sol.

- a. Hydrogen sometimes ignites with the large amount of heat released when water is absorbed by conc. H<sub>2</sub>SO<sub>4</sub>.
- b. Mn<sub>2</sub>O<sub>7</sub> is formed when KMnO<sub>4</sub> is dissolved in conc. H<sub>2</sub>SO<sub>4</sub>. Mn<sub>2</sub>O<sub>7</sub> formed is highly unstable and explosive in nature.

$$2KMnO4 + 2H2SO4 \longrightarrow K2SO4 + (MnO3)2SO4 + 2H2O$$

$$(MnO3)2SO4 + H2O \longrightarrow Mn2O7 + H2SO4$$

# CONCEPT APPLICATION EXERCISE 3.1

- 1. An aqueous solution of a gas (X) gives the following reactions:
  - (a) It decolourises an acidified K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> solution.
  - (b) On boiling with H<sub>2</sub>O<sub>2</sub>, cooling it and then adding an aqueous solution of BaCl<sub>2</sub>, a precipitate insoluble in conc. HCl is obtained.
  - (c) On passing H<sub>2</sub>S in the solution, white turbidity is obtained.

Identify (X) and give equations for steps

(a), (b) and (c).

- 2. An inorganic halide (A) reacts with water to form two acids (B) and (C). (A) also reacts with NaOH to form two salts (D) and (E) which remain in solution. The solution gives white precipitate with both AgNO<sub>3</sub> and BaCl<sub>2</sub> solutions respectively. (A) is a useful organic reagent. Identify (A) to (E).
- 3. Name the following compounds:
  - (a) Oxides of sulphur:

(i)  $S_2O$  (ii)  $S_2O_3$  (iii)  $SO_4$  (iv)  $S_2O_7$ 

(b) Oxyacids of sulphur:

 $\begin{array}{ll} \text{(i)} \ \text{H}_2\text{SO}_2 & \text{(ii)} \ \text{H}_2\text{SO}_3 & \text{(iii)} \ \text{H}_2\text{S}_2\text{O}_4 & \text{(iv)} \ \text{H}_2\text{S}_2\text{O}_2 \\ \text{(v)} \ \text{H}_2\text{S}_2\text{O}_5 & \end{array}$ 

- (c) Sulphuric acids: (i)  $H_2S_2O_3$  (ii)  $H_2S_2O_7$
- (d) Thionic acids: (i)  $H_2S_2O_6$  (ii)  $H_2(S)_nO_6$
- (e) Peroxo acids: (i)  $H_2SO_5$  (ii)  $H_2S_2O_8$
- 4. Explain the following:
  - (a) An acidified K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> paper turns green when exposed to SO<sub>2</sub>.
  - (b) H<sub>2</sub>S acts only as reducing agent while SO<sub>2</sub> can act both as a reducing agent and an oxidising agent.
  - (c) SO<sub>2</sub> acts as a bleaching agent.
  - (d) Sugar turns black on addition of conc. H<sub>2</sub>SO<sub>4</sub>.
  - (e) Ozone destroys mercury meniscus.
  - (f)  $SF_6$  is known, but  $SH_6$  is not known.
- 5. What happens when:
  - (a) Ozone is passed through acidified stannous chloride solution
  - **(b)** Potassium iodide is heated with conc. H<sub>2</sub>SO<sub>4</sub>.
  - (c) Sulphur is boiled with caustic soda solution.
  - (d) Ozone reacts with potassium ferrocyanide solution.
  - (e) Ozone is treated with ethylene.
  - (f) Sulphur dioxide is bubbled through aqueous solution of copper sulphate in presence of potassium thiocyanate.
  - (g) Sulphur dioxide gas, water vapour and air are passed over heated sodium chloride.
  - (h) Sulphuric acid is treated with PCl<sub>5</sub>.
- 6. When sulphur is boiled with Na<sub>2</sub>SO<sub>3</sub>, a compound (X) is produced. (X) with excess of AgNO<sub>3</sub> solution gives a compound (Y) which is soluble in water and produces a black coloured sulphide (Z). Identify compounds (X), (Y) and (Z).

7. Identify the products (P + OT) in the following  $r_{eaction}$  sequence:

sequence:
$$\begin{array}{ccc}
H_2SO_4 & \xrightarrow{+A} & P & \xrightarrow{-'O'} & Q \\
\downarrow^{-H_2O} & & \downarrow^{+'O'} & & \downarrow^{+'O'} \\
T & S & R
\end{array}$$

- 8. The following compounds on complete hydrolysis at room temperature gives the products.
  - (i)  $SF_4$  (ii)  $H_2S_2O_8$ .

Identify the products which acts as:

- (a) Dibasic acid
- (b) Monodentate ligand
- (c) Flexidentate ligand
- (d) Both oxidising and reducing agents.
- (e) Non-redox hydrolysis.
- 9. Complete the following equations:

i. 
$$(NH_4)_2S_2O_8 + H_2O + MnSO_4 \longrightarrow ..... + ..... + .....$$

ii. 
$$S + H_2SO_4(conc.) \xrightarrow{Heat} ..... + H_2O$$

iii. 
$$I_2 + SO_2 + H_2O \longrightarrow SO_4^{2-} + \dots + H^{\oplus}$$

iv. 
$$I_2 + O_3 + H_2O \longrightarrow HIO_3 + \dots$$

v. 
$$\operatorname{Cr}_2 \operatorname{O}_7^{2-} + \operatorname{H}^{\oplus} + \operatorname{SO}_2 \longrightarrow \operatorname{SO}_4^{2-} + \operatorname{H}_2 \operatorname{O} + \dots$$

vi. 
$$H_2S + HNO_3 \longrightarrow ..... + H_2O + S$$

- 10. An organic acid (A) reacts with concentrated H<sub>2</sub>SO<sub>4</sub> to give a neutral oxide (B), acidic oxide (C) and a diatomic oxide (D). When (D) reacts with chlorine gas, a poisonous gas (E) is evolved. This gas with ammonia gives an organic compound (F). The compounds (A) and (F) are
- 11. Compounds A and B are treated with dilute HCl separately. The gases liberated are Y and Z respectively. Y turns acidified K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> paper green while Z turns lead acetate paper black. The compounds A and B are respectively:
- 12. (i) The following oxides are given, if x = number of neutral oxides.

- (ii) The general formula for polythionic acid series  $H_2S_vO_6$ . If y is the value for hexathionic acid.
- (iii) If z is number of SOS bond in  $S_3O_9$  then calcute the value of expression x + y z.

# **Solved Examples**

#### EXAMPLE 3.1

State with balanced equation what happens when?

- a. Potassium ferrocyanide is heated with conc. H<sub>2</sub>SO<sub>4</sub>:
- b. A mixture of potassium chlorate, oxalic acid and sulphurit acid is heated.
- c. Sodium chlorate reacts with sulphur dioxide.
- d. Chlorine gas is passed into water saturated with hydroged sulphide.
- e. Hydrogen sulphide is passed through sodium bisulphile solution.



a. CO is evolved.

$$K_4 \text{Fe(CN)}_6 + 6\text{H}_2 \text{SO}_4 + 6\text{H}_2 \text{O} \xrightarrow{\Delta} \\ 2\text{K}_2 \text{SO}_4 + \text{FeSO}_4 + 3(\text{NH}_4)_2 \text{SO}_4 + 6\text{CO} \uparrow$$

b. Potassium chlorate is reduced while oxalic acid is oxidised.  $KClO_3 + H_2SO_4 \longrightarrow KHSO_4 + HCl + 3[O]$ 

$$_{3\text{H}_2\text{C}_2\text{O}_4}$$
 +  $_{3\text{E}_2\text{O}_4}$  +  $_$ 

$$\overline{\text{KClO}_3} + 3\text{H}_2\text{C}_2\text{O}_4 + \text{H}_2\text{SO}_4 \longrightarrow \text{KHSO}_4 + \text{HC1} + 6\text{CO}_2 + 3\text{H}_2\text{O}_4$$

c. NaClO<sub>3</sub> is reduced to NaCl.

$$SO_2 + 2H_2O \longrightarrow H_2SO_4 + 2[H] \times 3$$
  
NaClO<sub>2</sub> + 6[H]  $\longrightarrow$  NaCl + 3H<sub>2</sub>O

$$NaClO_3 + 3SO_2 + 3H_2O \longrightarrow 3H_2SO_4 + NaCl$$

d. 
$$Cl_2 + H_2S \longrightarrow 2HCl + S$$

e. 
$$2NaHSO_3 \longrightarrow Na_2SO_3 + H_2O + SO_2$$

$$SO_2 + 2H_2S \longrightarrow 2H_2O + 3S$$

$$\frac{1}{2NaHSO_3 + 2H_2S} \longrightarrow Na_2SO_3 + 3S + 3H_2O$$

### EXAMPLE 3.2

When gas A is passed through dry KOH at low temperature, a deep red coloured compound, B and a gas care obtained. The gas A, on reaction with but-2-ene, followed by treatment with Zn/H<sub>2</sub>O yields acetaldehyde. Identify A, B and C.

Sol. The reaction of gas A with but-2-ene followed by treatment with  $Zn/H_2O$  suggests that A is  $O_3$ .

Reaction with KOH

$$2KOH + 5O_3 \longrightarrow 2KO_3 + 5O_2 + H_2O$$
(A) (B) (C)

(Deep red coloured)

Hence A is  $O_3$ , B is  $KO_3$  and C is  $O_2$ .

#### EXAMPLE 3.3

- a. Sulphur melts to form a clear mobile liquid at 119°C but on further heating to 180°C, it becomes viscous. Why?
- b. SOCl<sub>2</sub> can act as a weak Lewis acid as well as a weak Lewis base. Explain.

#### Sol

- a. Up to 119°C, sulphur exists as S<sub>8</sub> molecules which can roll over one another to form a mobile liquid. However, when this liquid is further heated to 180°C, the cleavage of ring structure occurs and zig-zag open chains are formed which get interwound and tangled together and hence sulphur becomes more viscous.
- b. Like nitrogen in ammonia, sulphur has two lone pair of electrons which it can donate, hence it acts as a weak base.
  SOCl<sub>2</sub> has also empty d-orbitals which can accommodate electron pairs from bases and hence acts as a weak acid.

### EXAMPLE 3.4

Concentrated H<sub>2</sub>SO<sub>4</sub> is added to the test tubes containing (a) to (e)

Test tube	Compounds		
a.	Cane sugar		
b.	Sodium bromide		
C.	Copper turnings		
d.	Sulphur powder		
e.	Potassium chloride		

Identify in which of the above test tubes, the following change will be observed on heating. Also give the chemical equations involved.

- i. Formation of black substance.
- ii. Evolution of brown gas.
- iii. Evolution of colourless gas.
- iv. Formation of brown substance, which on dilution becomes blue.
- v. Disappearance of yellow powder along with the evolution of a colourless gas.

#### Sol.

i. Conc. H<sub>2</sub>SO<sub>4</sub> + Cane sugar → Black substance Conc. H<sub>2</sub>SO<sub>4</sub> acts as a dehydrating agent, hence it removes water from cane sugar on heating and forms a black substance known as sugar charcoal.

$$C_{12}H_{22}O_{11} \xrightarrow{\text{Conc. } H_2SO_4} 12C + 11H_2O$$

Thus, formation of black substance occurs in test + tube (a).

ii. Conc. H<sub>2</sub>SO<sub>4</sub> + sodium bromide → Brown gas On heating NaBr along with conc. H<sub>2</sub>SO<sub>4</sub>, brown gas Br<sub>2</sub> is evolved. Initially HBr is produced, as HBr is a moderate reducing agent, it reduces H<sub>2</sub>SO<sub>4</sub> to SO<sub>2</sub> and itself is oxidised to bromine gas, Br<sub>2</sub>.

$$2\text{NaBr} + \text{H}_2\text{SO}_4 \xrightarrow{\Delta} \text{Na}_2\text{SO}_4 + 2\text{HBr}$$

$$2HBr + H_2SO_4 \xrightarrow{\Delta} Br_2 + SO_2 + 2H_2O$$

$$\frac{1}{2NaBr + H_2SO_4 \longrightarrow Na_2SO_4 + Br_2 + SO_2 + 2H_2O_4}$$

Thus, evolution of brown gas occurs in test tube (b).

iii. Potassium chloride + conc. H<sub>2</sub>SO<sub>4</sub> → colourless gas KCl on heating with conc. H<sub>2</sub>SO<sub>4</sub>, liberates HCl gas which is colourless.

$$2KCl + H_2SO_4(conc.) \xrightarrow{\Delta} K_2SO_4 + 2HCl$$

Since HCl is not a reducing agent, it does not reduce H<sub>2</sub>SO<sub>4</sub> to SO<sub>2</sub>. Thus evolution of colourless gas occurs in test tube (e).

iv. Cu turnings + conc.  $\xrightarrow{\Delta}$  Brown substance  $\xrightarrow{\text{H}_2\text{O}}$ 

Blue soln.

$$Cu + 2H_2SO_4 \xrightarrow{\Delta} CuSO_4 + SO_2 + H_2O$$
Anhydrous

copper sulphate

$$CuSO_4 + 5H_2O \xrightarrow{\Delta} CuSO_4 \cdot 5H_2O$$
Blue

On heating, Cu turnings with conc. H<sub>2</sub>SO<sub>4</sub>, a brownish substance, i.e. a mixture of Cu turnings and white anhydrous copper sulphate is formed along with evolution of pungent smelling  $\mathrm{SO}_2$  gas. On dilution, the solution turns blue due to the formation of hydrated copper sulphate which is soluble in water. Hence, formation of brown substance, which on dilution becomes blue occurs in test tube (c).

v. Sulphur powder + conc. 
$$H_2SO_4 \xrightarrow{\Delta}$$

$$[H_2SO_4 \xrightarrow{\Delta} H_2O + SO_2 + [O]] \times 16$$

$$S_8 + 16[O] \longrightarrow 8SO_2$$

$$S_8 + 16H_2SO_4 \longrightarrow 24SO_2 + 16H_2O$$
Yellow
Colourless
powder
powder
Smelling gas

v. On heating sulphur powder, which is yellowish in colour with conc. H<sub>2</sub>SO<sub>4</sub>, pungent smelling colourless, SO<sub>2</sub> gas is produced, thus yellow powder disappears and the above reaction will occur in test tube (d).

#### EXAMPLE 3.5

A pale yellow substance (A) when heated with conc. HNO evolves a brown coloured gas (B). The substance (A) also dissolves in sodium sulphite solution on heating. A clear solution (C) is formed which on acidification gives a turbid solution and a pungent smelled gas (D) which is formed by the substance (A) in air. The solution (C) decolourises iodine solution. Identify (A) to (D).

#### Sol.

$$(A) \xrightarrow{\text{Conc. HNO}_3} (B)$$
Heat  $Na_2SO_3$  Brown coloured gas
$$(A) \text{ dissolve}$$
to form  $(C)$  Acidification Turbid + Pun

to form (C) 
$$\xrightarrow{\text{Acidification}}$$
 Turbid + Pungent smelling solution gas (D)

$$(A) \xrightarrow{an} (D)$$

(C) soln. + 
$$I_2$$
 soln.  $\longrightarrow$  Decolourisation of  $I_2$  soln.

Pale yellow substance (A) is sulphur.

S + 6HNO<sub>3</sub> (conc.) 
$$\xrightarrow{\Delta}$$
 H<sub>2</sub>SO<sub>4</sub> + 2H<sub>2</sub>O + 6NO<sub>2</sub>↑

(B)

brown coloured gas

$$S + Na_2SO_3 \xrightarrow{\Delta} Na_2S_2O_3$$

Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>, on acidification, gives a turbid solution and a pungent smelling gas due to formation of S and SO<sub>2</sub> respectively.

$$Na2S2O3 + H2SO4 \longrightarrow NaSO4 + SO2 + S \downarrow + H2O$$
(C)
(D)

$$S + O_2 \longrightarrow SO_2$$
(A) (air) (D)

$$2Na_2S_2O_3 + I_2 \longrightarrow Na_2S_4O_6 + 2NaI$$
Colourless solution

Since  $I_2$  is reduced to  $I^{\Theta}$ , a colourless solution is formed.

### EXAMPLE 3.6

In the following oxyanions:

i. 
$$SO_4^{2-}$$
 ii.  $S_2O_5^{2-}$  iii.  $S_2O_7^{2-}$  iv.  $S_3O_6^{2-}$ 

If X = Number of oxyanions having two equivalent  $S - O_{bohd_s}$ per central atom.

Y = Number of oxyanions having three equivalent S-O bondsper central atom.

Z = Number of oxyanions having four equivalent S-O  $b_{Ond_0}$ per central atom.

Find the value of X + Y + Z.

#### Sol.

Oxyanions Sulphate ion (SO <sub>4</sub> <sup>2-</sup> )	No. of equivalent bonds
	X = 2
ii. Pyrosulphite ion $(S_2O_5^2)$ O O S S S O O O O	X = 2 $Y = 3$
iii. Pyrosulphate ion $(S_2O_7^{2-})$ O O S S S O O O O O O O O O O	Y = 3
iv. Trithionate ion $(S_3O_6^{2-})$ $ \begin{array}{ccc} O & O \\ S & S \\ O & O \end{array} $	Y = 3
X + Y + Z = (2 + 2) + (3	+3+3)+0-12

## EXAMPLE 3.7

The oxyacid are represented as  $Hx_1S_2Ox_2$ , where  $x_1$  and  $x_2$  are natural numbers.

If there are three possible oxyacid of sulphur, A, B and C and ratio of  $x_2$ :  $x_1$  are 2, 3 and 4 respectively. Calculate the sum of oxidation state of 'S' atom in three oxyacids.

**Sol.** For any oxyacid of 'S' atom number of H-atom = 2.

Formula of oxyacids would be:

 $\begin{array}{c} {\rm H}x_1{\rm S}_2{\rm O}x_2 \Rightarrow {\rm H}_2{\rm S}_2{\rm O}_3, \ {\rm H}_2{\rm S}_2{\rm O}_4, \ {\rm H}_2{\rm S}_2{\rm O}_5, \ {\rm H}_2{\rm S}_2{\rm O}_6, \ {\rm H}_2{\rm S}_2{\rm O}_7, \\ {\rm H}_2{\rm S}_2{\rm O}_8 \ {\rm and \ so \ on.} \end{array}$ 

For 
$$H_2S_2O_4$$
;  $\frac{x_2}{x_1} = \frac{4}{2} = 2$ 

Oxidation state (O.S.) of 'S' = +3

For 
$$H_2S_2O_6$$
;  $\frac{x_2}{x_1} = \frac{6}{2} = 3$ 

O.S. of 'S' atom = 
$$+4$$

For H<sub>2</sub>S<sub>2</sub>O<sub>8</sub>; 
$$\frac{x_2}{x_1} = \frac{8}{2} = 4$$
  
O.S. of 'S' atom = +6

Sum of O.S. = 
$$3 + 4 + 6 = 13$$

# EXAMPLE 3.8

The general formula of polythionate ion is  $S_{n+2}O_6^{2-}$ . If average oxidation state of 'S' atom in any polythionate ion is equal to bond order of 'S-O' bond. Then calculate the value of 'n' for the corresponding polythionate ion.

# Sol. Structure of polythionate ion is:

$$\begin{array}{c} O \\ S \\ S \\ -+5 \\ O \end{array} \\ \begin{array}{c} O \\ S \\ O \end{array} \\ \begin{array}{c} O \\ S \\ O \end{array} \\ \begin{array}{c} O \\ S \\ O \end{array} \\ \begin{array}{c} O \\ O \\ O \\ \end{array} \\ \begin{array}{c} O \\ O \\ O \\ \end{array} \\ \begin{array}{c} O \\ O \\ O \\ \end{array} \\ \begin{array}{c} O \\ O \\ O \\ \end{array} \\ \begin{array}{c} O \\ O \\ O \\ \end{array}$$

(No. of resonating structure = 3)

Resonating structures are:

(Similar resonating structures are obtained from 'S' atom 'b' therefor total resonating structures = 3.

(Two bonded atoms selected as 1 and 2).

Bond order = 
$$\frac{\text{Total no. of bonds between two}}{\text{Total no. of resonating structures}}$$

(Any two bonded atoms may be selected and a double bond will mean two bonds and a triple bond means three bonds).

Bond order = 
$$\frac{\text{Double bond in (I) + Double bond in (II)}}{\text{Total resonating structures}}$$
$$= \frac{2(\text{in I}) + 2(\text{in III}) + 1(\text{in II})}{3}$$
$$= \frac{5}{3} = 1.66.$$

$$\therefore$$
 Bond order of (S-O) bond = 1.66 or  $\left(\frac{5}{3}\right)$ 

Average O.S of 'S' atom = 
$$\frac{\text{Total O.S.}}{\text{No. of S-atom}}$$
  
=  $\frac{+5+5}{n+2} = \frac{10}{n+2}$ 

Thus 
$$\frac{10}{n+2} = \frac{5}{3}$$
 (Bond order)

$$n + 2 = 6$$

$$n = 4$$
.

#### EXAMPLE 3.9

Peroxydisulphuric acid (A) on partial hydrolysis gives two acid (X) and (Y).

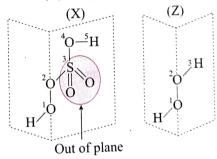
Acid (X) on hydrolysis a compound (Z) and acid (Y).

If Q and R represent maximum number of atoms that can lie in a plane of acid (X) and compound (Z).

Then find the value of  $\frac{Q+R}{2}$ 

Sol. 
$$H_2S_2O_8 + H_2O \longrightarrow H_2SO_5 + H_2SO_4$$
(A) (X) (Y)
$$H_2SO_5 + H_2O \longrightarrow H_2O_2 + H_2SO_4$$
(X) (Z) (Y)

Structures of (X) and (Z) are:



No. of atoms in a plane = 5 = Q

No. of atoms in a plane = 3 = R

$$\therefore \quad \frac{Q+R}{2} = \frac{5+3}{2} = 4$$

# **Exercises**

# Single Correct Answer Type

# Physical and Chemical Properties

- 1. Which one of the following has the highest bond energy?
  - (1) O O

- (2) S-S
- (3) Se-Se
- (4) Te-Te
- 2. Which one has the highest and lowest boiling point?
  - $(1) H_{2}O, H_{2}S$
- (2) H<sub>2</sub>O, H<sub>2</sub>Se
- $(3) H_{2}S, H_{2}O$
- (4) H<sub>2</sub>S, H<sub>2</sub>Se
- 3. Which one of the following is strongest acid?
  - $(1) H_{2}S$

(2) H<sub>2</sub>Se

- $(3) H_{2}O$
- (4) H, Te
- 4. Which one has the lowest boiling point?
  - $(1) H_{2}O$

- $(2) H_{2}S$
- (3) H<sub>2</sub>Se

- (4) KNO<sub>3</sub>
- 5. Anomalous behaviour of oxygen is due to
  - (1) It is highly electronegative
  - (2) Small atomic size
  - (3) Non- availability of d-orbitals
  - (4) All
- **6.** Which shows maximum catenation property?
  - (1) Se

(2) Te

(3) Po

- (4) S
- 7. Which one of the following is wrong?
  - (1) Oxygen and sulphur belong to the same group of periodic table
  - (2) Oxygen is a gas while sulphur is solid
  - (3) Both oxygen and sulphur show +2, +4 and +6 oxidation states
  - (4) H<sub>2</sub>S has no hydrogen bonding
- 8. Non-metals combine with oxygen to form usually
  - (1) Basic oxides
- (2) Neutral oxides
- (3) Acidic oxides
- (4) Amphoteric oxides
- 9. Sulphur does not exist as S<sub>2</sub> molecule because
  - (1) It is less electronegative
  - (2) It has ability to exhibit catenation
  - (3) It is not able to constitute  $p\pi p\pi$  bond
  - (4) It has the tendency to show variable oxidation states
- 10. The element evolving two different gases on reaction with conc. H<sub>2</sub>SO<sub>4</sub>
  - (1) P

(2) C

(3) Hg

- (4) S
- 11. Sulphur reacts with chlorine in 1: 2 ratio and forms (X). (X) on hydrolysis gives a sulphur compound (Y). What is the hybridised state of central atom in the anion of (Y)?
  - (1) sp

 $(2) sp^{3}$ 

(3)  $sp^2$ 

 $(4) sp^3 d$ 

- 12. Gas that cannot be collected over water is:
  - $(1) N_2$

 $(2)O_{2}$ 

(3) SO<sub>2</sub>

- (4) PH<sub>3</sub>
- 13. One gas bleaches the colour of flowers by reduction,  $w_{h||_0}$ the other by oxidation, the two gases respectively are.
  - (1) CO and Cl<sub>2</sub>
- (2) NH<sub>3</sub> and SO<sub>2</sub>
- (3) H<sub>2</sub>S and Br<sub>2</sub>
- (4) SO<sub>2</sub> and Cl<sub>2</sub>
- 14. Which pair of elements can form multiple bond with itself and oxygen?
  - (1) F, N

(2) N, CI

(3) N, P

- (4) N, C
- 15. Which of the following is the correct order of melting points of group 16 elements?
  - (1) O < S < Se < Te < Po
- (2)  $O < S < Se < Te \approx P_0$
- (3) O < S < Se < Te > Po
- (4)  $O < S < Se > Te < P_0$
- 16. Which of the following elements(s) are known as photosensitive elements?
  - (1) Te

- (2) Se
- (3) Both (1) and (2)
- (4) None of these
- 17. The correct order of acidic nature of trioxide is
  - $(1) SO_3 > SeO_3 > TeO_3$
- (2) SO<sub>3</sub> > TeO<sub>3</sub> > SeO<sub>3</sub>
- (3)  $\text{TeO}_3 > \text{SO}_3 > \text{SeO}_3$ 
  - (4) SO<sub>3</sub> < SeO<sub>3</sub> < TeO<sub>3</sub>
- 18. Which of following represents the correct order of melting point of hydrides of group-16?
  - (1)  $H_2O > H_2S > H_2Se > H_2Te$
  - $(2) H_2O > H_2S > H_2Te > H_2Se$
  - $(3) H_2O > H_2Te > H_2Se > H_2S$
  - (4)  $H_2O > H_2Se > H_2Te > H_2S$
- 19. Stability of tetrabromides follows the order

  - (1)  $SeBr_4 < TeBr_4 < PoBr_4$  (2)  $SeBr_4 < PoBr_4 < TeBr_4$
  - (3) PoBr<sub>4</sub> < TeBr<sub>4</sub> < SeBr<sub>4</sub>
- (4) None of these
- 20. Correct order of hydrolysis of hexa-fluorides is
  - (1)  $TeF_6 > SeF_6 > SF_6$
- $(2) SF_6 > SeF_6 > TeF_6$
- (3)  $SF_6 > TeF_6 > SeF_6$
- (4) None of these
- 21. Which of the following is correctly represents increasing order of reducing nature of hybrids?

- $\begin{array}{ll} (1) \ H_2S < H_2Se < H_2Te \\ (3) \ H_2Se < H_2S < H_2Te \\ \end{array} \qquad \begin{array}{ll} (2) \ H_2S < H_2Te < H_2S \\ (4) \ H_2Te < H_2Se < H_2Se \\ \end{array}$  $(4) H_{2}Te < H_{2}Se < H_{2}S$

# Compounds of Oxygen

- 22. Which of the following compounds does not evolve oxygen when heated alone?
  - (1) KClO<sub>3</sub>
- $(2) \text{ KMnO}_{4}$
- (3) NH<sub>4</sub>NO<sub>2</sub>
- (4) KNO<sub>3</sub>
- 23. When oxygen is passed through a solution of Na<sub>2</sub>SO<sub>3</sub>, we get
  - (1) Na<sub>2</sub>S

- (2) Na<sub>2</sub>SO<sub>4</sub>
- (3) NaHSO<sub>4</sub>
- (4) NaH
- **24.** The product A in the following reaction:
  - $2KMnO_4 \longrightarrow A + KMnO_2 + O_2$  is

- $(1) K_2 M n_2 O_7$
- $(2) K_2 MnO_4$
- $(3) K_2O$

- $(4) K_2 O_2$
- 25. The gases respectively absorbed by alkaline pyrogallol and oil of cinnamon is
  - $(1) O_3, CH_4$
- (2) SO<sub>2</sub>, CH<sub>4</sub>
- $(3) O_2, O_3$
- $(4) N_2O, O_3$
- 26. Ozone reacts with K<sub>4</sub>Fe(CN)<sub>6</sub> to form  $(1) Fe_2O_3$ 
  - (2) Fe(OH)<sub>3</sub>
  - (3) Fe(OH),
- (4) K<sub>3</sub>Fe(CN)<sub>6</sub>
- 27. Which one of the following is **not true** peroxide?
  - (1) PbO,

- (2) BaO<sub>2</sub>
- (3) Na<sub>2</sub>O<sub>2</sub>
- $(4) H_2O_2$
- 28. Which one of the following is an amphoteric oxide?
  - (1) MnO,
- (2) ZnO

(3) CaO

- (4) CO<sub>2</sub>
- 29. On heating ozone, its volume
  - (1) Increases to 1.5 times
- (2) Decreases to half
- (3) Remain unchanged
- (4) Becomes double
- 30. In the reaction,

$$2KI + H_2O + O_3 \longrightarrow 2KOH + O_2 + A$$
  
the compound A is

(1) KIO<sub>3</sub>

(3) HIO<sub>3</sub>

- 31. Select the **incorrect** statement about the following:
  - (1) O<sub>3</sub> is used as germicide for purification of air
  - (2) In O<sub>3</sub>, O—O bond length is identical with that of molecular oxygen
  - (3) O<sub>3</sub> molecule is angular in shape
  - (4) O<sub>3</sub> is an oxidising agent
- 32. The correct order of O—O bond length in  $O_2$ ,  $H_2O_2$  and  $O_3$ 
  - $(1) O_3 > H_2O_2 > O_2$
- (2)  $O_2 > H_2O_2 > O_3$
- $(3) O_2 > O_3 > H_2O_2$
- (4)  $H_2O_2 > O_3 > O_2$
- 33. Which of the following is not correct?
  - (1)  $3O_2 = \frac{\text{Silent electric}}{\text{Discharge}} 2O_3$ ;  $\Delta H = -284.5 \text{ kJ}$
  - (2) Ozone undergoes addition reaction with unsaturated carbon compounds.
  - (3) Sodium thiosulphate reacts with  $I_2$  to form sodium tetrathionate and sodium iodide.
  - (4) Ozone oxidises lead sulphide to lead sulphate
- 34. Tailing of mercury test can be used for which of the following gas?
  - (1) Dioxygen
- (2) Dihydrogen
- (3) Dinitrogen
- (4) Ozone
- 35. Which gas is used to improve the atmosphere of the crowded places?
  - $(1) H_{2}$

(2)  $O_2$ 

 $(3) O_3$ 

- $(4) N_2O$
- 36. By which of the following methods,  $H_2O_2$  can't synthesized?
  - (1) Aerial oxidation of 2-ethyl anthraquinol

- (2) Addition of ice cold H<sub>2</sub>SO<sub>4</sub> on PbO<sub>2</sub>
- (3) Lewis addition of ice cold H<sub>2</sub>SO<sub>4</sub> on BaO<sub>2</sub>
- (4) Electrolysis of (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> at a high current density
- 37. Estimation of ozone can be made quantitatively by
  - (1) Decomposition into  $O_2$  and absorption of  $O_2$  into pyrogallol
  - (2) Volumetric method using KI and titration of the liberated iodine using hypo solution
  - (3) Oxidative ozonolysis method
  - (4) All methods give above
- 38. A green coloured solution of same salt changes its colour to light pink on passing ozone through it. Which of the following species represent pink and green colour respectively? (1)  $MnO_4^{\ 2-}$  and  $MnO_4^{\ -}$ (2)  $Mn^{2+}$  and  $MnO_2$ (3)  $MnO_4^{\ -}$  and  $MnO_4^{\ 2-}$ (4)  $Cu^+$  and  $Cu^{2+}$

- 39. Which of the following reaction is carried out to obtain pure oxygen?
  - (1) By the action of water on oxone
  - (2) By heating alkali nitrates
  - (3) By heating  $KMnO_4$  or  $K_2Cr_2O_7$  with conc.  $H_2SO_4$
  - (4) By adding H<sub>2</sub>O<sub>2</sub> to acidified KMnO<sub>4</sub> solution

# Compounds of Sulphur

- 40. Which has greater reactivity
  - (1) TeCl<sub>6</sub>
- (2)  $SF_6$

- (3) TeF<sub>6</sub>
- (4) SeF<sub>6</sub>
- 41. SO<sub>3</sub> exists in
  - (1) 3 forms
- (2) 2 forms (4) Only one
- (3) 4 forms
- **42.** H<sub>2</sub>SO<sub>3</sub> and H<sub>2</sub>SO<sub>4</sub> involve hybridisation of the type
  - (1) Both  $sp^3$
- (2) Both  $sp^3d$
- $(3) sp^3, sp^3d$
- (4) Both  $dsp^2$
- 43. Sulphuric acid has great affinity for water because it (2) Forms hydrate with water
  - (1) Decomposes water
- (4) Decomposes the acid
- (3) Hydrolyse the acid
- **44.** High density arid low volatility of H<sub>2</sub>SO<sub>4</sub> is due to (2) van der Waals force
  - (1) Strong bonds (3) Hydrogen bonding
- (4) None
- **45.** Conc. H<sub>2</sub>SO<sub>4</sub> is not a
  - (1) Dehydration agent
- (2) Hygroscopic (4) Efflorescent
- (3) Oxidising agent
- **46.** In the following reaction, H<sub>2</sub>SO<sub>4</sub> acts as  $HCOOH \xrightarrow{H_2 \overrightarrow{SO_4}} CO + H_2O$

(1) Dehydrating agent

- (2) Oxidising agent (4) All
- (3) Reducing agent
- 47. Oxalic acid when heated with conc. H<sub>2</sub>SO<sub>4</sub> it gives out
  - (1) H<sub>2</sub>O and CO<sub>2</sub>
- (2) Oxalic sulphate
- (3)  $CO_2$  and  $H_2S$
- (4) CO and CO,
- **48.** In the following reaction,  $H_2SO_4$  acts as  $2Ag + H_2SO_4 \longrightarrow Ag_2SO_4 + 2H_2O + SO_2$

3.34 Inorganic Chemistry		61	1. The number of sigma and pi bonds in peroxydisulphuric acid
(1) Reducing agent	(2) Oxidising agent	0.1	are, respectively
	(4) Dehydration agent		(1) 9 and 4 (2) 11 and 4 (4) 4 and 9
	a few drops of conc. H <sub>2</sub> SO <sub>4</sub> on his part blackens and holes appears.		(3) 4 and 8
entrop chirt and spiasica		62	2. Which of the following solutions does not change its colour
This is because the sulphu	He acid		on passing ozone through it?
(1) Heats up the cotton so	mat it burns		(1) Starch iodide solution
<ul><li>(2) Dehydrates the cotton</li><li>(3) Causes the cotton to re</li></ul>	pact with oxygen in air		(2) Alcoholic solution of benzidine
(4) Removes the elements	of water from cotton		(3) Acidic solution of K <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub>
(4) Removes the elements	shy because of its		(4) Acidified solution of FeSO <sub>4</sub>
50. Hypo is used in photograp	(2) Solubility in water	63	3. Hydrolysis of one mole of peroxydisulphuric acid
(1) Complexing ability	(4) Sensitivity to light		produces
(3) Reducing behaviour	d does not react with		(1) Two moles of sulphuric acid (2) Two moles of peroxymonosulphuric acid
51. Caro's and Marshall's acid	(2) KMnO <sub>4</sub>		(2) Two moles of peroxyments and one mole of peroxy (3) One mole of sulphuric acid and one mole of peroxy
(1) S	(4) H <sub>2</sub> O		(3) One mole of sulphuric acid
(3) KI	the action of dilute H <sub>2</sub> SO <sub>4</sub> on:		of sulphuric acid, one mole of peroxymono
52. Sulphur dioxide is obtaine	ed by the action of dilute H <sub>2</sub> SO <sub>4</sub> on:  (2) Sodium sulphate		sulphuric acid and one mole of flydrogen peroxide
(1) Copper turning	(4) Sodium sulphide	64	with an an inorganic compound reacts with SO <sub>2</sub> in aqueou
(3) Sodium sulphite		04.	diam produces (A). (A) on reaction with Na <sub>2</sub> CO <sub>2</sub> give
53. Moist iodine reacts with o	(2) I2O5		the compound (B) which with sulphur gives a substance (C
(1) HI	(4) $\text{HIO}_4$		used in photography. The compound (C) is
(3) HIO <sub>3</sub>	tained on dehydration of HCOOH		(1) $Na_2S_2O_3$ (2) $Na_2SO_4$
54. The ratio of the gases out and $H_2C_2O_4$ by conc. $H_2S$	O. is		(3) $Na_2S_2O_7$
(1) 2:1	(2) 1 : 2	65.	Identify the correct sequence of increasing number
(3) 3 : 1	(4) 1 : 3		$\pi$ -bonds in structures of the following molecules.
55. When SO <sub>2</sub> is passed throu			(I) $H_2S_2O_6$ (II) $H_2SO_3$ (III) $H_2S_2O_5$
(1) Sulphuric acid is forms	ed (2) A clear solution is formed		$(1) I, II, III \qquad (2) II, III, I$
(3) Sulphur is precipitated	(4) No change is observed		(3) II, I, III (4) I, III, II
<b>56.</b> SF <sub>6</sub> is unreactive towards		66.	. Which of the following reactions depict the oxidizing
(1) Sulphur has very small			behaviour of H <sub>2</sub> SO <sub>4</sub> ?
(2) Fluorine is most electro			$(1) 2NaOH + H2SO4 \longrightarrow NaSO4 + 2H2O$
(3) Sulphur shows +6 oxid			(2) $2PCl_5 + H_2SO_4 \longrightarrow 2POCl_3 + 2HCl + SO_2Cl_2$
	, molecule cannot attack S-atom		(3) $2HI + H_2SO_4 \longrightarrow I_2 + SO_2 + 2H_2O$
57. From the following information			(4) NaCl + $H_2SO_4 \longrightarrow NaHSO_4 + HCl$
$X + H_2SO_4 \longrightarrow Y$ (a colou		67	The oxidation state of sulphur in the anions $SO_3^{2-}$ and $S_2O_3$
$X + H_2SO_4 \longrightarrow I$ (a colour	green coloured solution	07.	follows the order:
$Y + K_2Cr_2O_7 + H_2SO_4 \longrightarrow$	green coloured solution		(1) $S_2O_4^{2-} < S_2O_6^{2-} < SO_3^{2-}$ (2) $S_2O_4^{2-} < SO_3^{2-} < S_2O_6^{2-}$
Identify the pair X and Y.	(2) CO <sup>2-</sup> CO		$(1)3_20_4 \times 3_20_6 \times 30_3 \times (2)3_20_4 \times 30_2 \times (2)3_20_4 \times (2)3_20$
(1) CI <sup>⊖</sup> , HCl	(2) $SO_3^{2-}$ , $SO_2$		(3) $SO_3^{2-} < S_2O_4^{2-} < S_2O_3^{2-}$ (4) $S_2O_6^{2-} < SO_4^{2-} < SO_3^{2-}$
(3) $S^{2-}$ , $H_2S$	(4) $CO_3^{2-}$ , $CO_2$	68.	. In presence of moisture, SO <sub>2</sub> acts as a good reducing age
3. Which one of the following	statements is wrong?		Which of the following statement is correct.
(1) SO <sub>2</sub> dissolves in water ar	nd forms sulphurous acid		(1) It turns orange coloured potassium dichromate soluti
(2) SO <sub>2</sub> acts as a bleaching a			green.
(3) SO <sub>2</sub> has pungent odour			(2) It decolourises pink violet colour of acidified KMn
(4) SO <sub>2</sub> acts only as oxidisin	g agent		solution, as SO <sub>2</sub> reduces MnO <sub>4</sub> <sup>-</sup> to Mn <sup>2+</sup>
Which of the following acts a			(3) Both (1) and (2)
(1) HNO <sub>3</sub>	(2) H <sub>2</sub> SO <sub>4</sub>		(4) None of these
(3) HCl	(4) HNO <sub>2</sub>	69.	. Which of the following halides cannot be hydrolyzed
	2		room temperature?
Excess of PCl <sub>5</sub> reacts with co			(I) $TeF_6$ (II) $SF_6$
(1) Sulphuryl chloride	(2) Sulphurous acid		(III) NCl <sub>3</sub> (IV) NF <sub>3</sub>
(3) Chlorosulphonic acid	(4) Thionyl chloride		, , ,
			*

Choose the correct code:
(1) III and IV
(3) I, II and IV
(3) = , and an

(2) I, II and III

(4) II and IV

- 70. Give the correct order of initials T or F for following statements. Use T if statement is true and F if it is false.
  - (1) Number of S—S bonds in  $H_2S_nO_6$  are (n+1)
  - (II) When F<sub>2</sub> reacts with water gives HF, O<sub>2</sub> and O<sub>3</sub>
  - (III) LiNO3 and BaCl2 compounds are used in fire works
  - (IV) Be and Mg hydrides are ionic and polymeric
  - (1) FTTF

- (2) TTFF
- (3) FTTT
- (4) TFTT
- 71. Which of the following parent oxyacid does not have its hypo acid?
  - (1) HNO,
- (2) H<sub>2</sub>SO<sub>3</sub>
- (3) HClO<sub>3</sub>
- (4) H<sub>3</sub>PO<sub>3</sub>
- 72. Consider the following reactions:
  - (i)  $PCl_3 + 3H_2O \longrightarrow H_3PO_3 + 3HCl$
  - (ii)  $SF_4 + 3H_2O \longrightarrow H_2SO_3 + 4HF$
  - (iii)  $BCl_3 + 3H_2O \longrightarrow H_3BO_3 + 3HCl$
  - $(iv) XeF_6 + 3H_2O \longrightarrow XeO_3 + 6HF$

Then according to given information the incorrect statement

- (1) During the (iv) reaction the hybridization of 18th group element does not change
- (2) During the (iii) reaction the hybridization of 13th group element does not change
- (3) During the (ii) reaction the hybridization of 16th group element has been changed
- (4) During the (i) reaction the hybridization of 15th group element does not change
- 73. The correct order of S—S bond length in following oxyanions

  - (I)  $S_2O_4^{\ 2-}$  (II)  $S_2O_5^{\ 2-}$  (III)  $S_2O_6^{\ 2-}$
  - (1)  $I > \coprod > \coprod$
- (2) III > II > I
- (3) III > I > II
- (4)I > III > II
- 74. In which of the following reaction product does not contain 'Peroxy' linkage?
  - $(1) H_4 P_2 O_8 \xrightarrow{+H_2 O}$
- (2) 2 Na  $\xrightarrow{\text{excess O}_2}$
- (3) 2OF Dimerization —
- (4) None of these
- 75. Consider the following statements in respect of oxides of
  - (I) In gas phase SO<sub>2</sub> molecule is V-shape.
  - (II) In gas phase SO<sub>3</sub> molecule is planar.
  - (III)  $\gamma$ -SO<sub>3</sub> is cyclic trimer.
  - (1) I & II only
- (2) II and III only
- (3) I & III only .
- (4) I, II and III
- 76. In thiosulphuric acid:
  - (1) there is only one replaceable hydrogen atom
  - (2) one S atom is in +2 and other sulphur atom is in +4 oxidation state

- (3) there is a S=S linkage present
- (4) each sulphur atom is in identical oxidation state
- 77. The dipole moment of H<sub>2</sub>O<sub>2</sub> is more than that of H<sub>2</sub>O but H<sub>2</sub>O<sub>2</sub> is not a good solvent because.
  - (1) It acts as a reducing agent
  - (2) It does not acts as an oxidizing agent
  - (3) It dissociates easily and acts as oxidizing agent in chemical reactions
  - (4) It has a very high dielectric constant so that ionic compounds cannot be dissolved in it.

## Multiple Correct Answers Type



## **Physical and Chemical Properties**

- 1. Oxygen has -1 oxidation state in the compound
  - (1) Caro's acid
- (2) Marshall's acid

(3) BaO<sub>2</sub>

- $(4) K_2O$
- 2. Oxygen has -2 oxidation state in the compound
  - (1) MgO

(2)  $F_2O$ 

(3) Na<sub>2</sub>O

- $(4) H_2O_2$
- 3. Select the correct statements about oxygen molecule.
  - (1) It is paramagnetic
  - (2) Its bond order is two
  - (3) Its liquid state it is colourless
  - (4) It has two unpaired electrons
- 4. Which reagent does not give oxygen as one of the products during oxidation with ozone?
  - (1) SO<sub>2</sub>

(2) SnCl<sub>2</sub>/HCl

 $(3) H_2S$ 

- (4) PbS
- 5. Which of the following elements form  $p\pi d\pi$  bonding in its oxide?
  - (1) Lithium
- (2) Boron
- (3) Sulphur
- (4) Nitrogen
- 6. Which of the following statement(s) is/are correct?
  - (1) Rhombic suplhur is stable at room temperature
  - (2) Monoclinic sulphur is stable at room temperature
  - (3) Both rhombic and monoclinic sulphur has the molecular formula S<sub>8</sub>
  - (4) Both rhombic and monoclinic sulphur are soluble in CS,
- 7. Identify the correct statements(s):
  - (1) Ozone is a powerful oxidizing agent as compared to O,
  - (2) Ozone reacts with KOH and gives an orange coloured solid KO3
  - (3) There is a decrease in volume when ozone decomposed to form O<sub>2</sub>
  - (4) The decomposition of O<sub>3</sub> to O<sub>2</sub> is exothermic
- 8. Which statements are correct for ozone?
  - (1) It is obtained by silent electric discharge on oxygen
  - (2) It can be obtained by the action of ultraviolet rays on oxygen (modified)
  - (3) It is regarded as an allotrope of oxygen
  - (4) Ozone molecules is paramagnetic like oxygen molecule

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- 9. Which of the following statements are correct regarding allotropes of Se?
  - (1) It shows three grey forms
  - (2) It shows three red non-metallic forms consisting of Se<sub>8</sub>
  - (3) The grey metallic forms contains infinite spiral chains of Se atoms with weak metallic interaction between adjacent chains.
  - (4) Grey Se is the only form which conducts electricity
- 10. Oxygen is evolved when:
  - (1) Zinc oxide is treated with NaOH
  - (2) Ammonium nitrate is heated
  - (3) Sodium peroxide reacts with conc. Acid
  - (4) Potassium superoxide reacts with H<sub>2</sub>O

#### Compounds of Oxygen and Sulphur

- 11. Solid SeO<sub>3</sub> (selenium trioxide) and TeO<sub>3</sub> exist respectively
  - (1) Cyclic trimer
  - (2) Cyclic tetramer
  - (3) Chain structure
  - (4) Three dimensional net work structure
- 12. Which among the following are peroxo acid of sulphur?
  - $(1) H_2SO_3$
- $(2) H_2 SO_5$
- $(3) H_{2}S_{2}O_{8}$
- (4) H<sub>2</sub>SO<sub>4</sub>
- 13. SO<sub>2</sub> acts as
  - (1) Bleaching agent
- (2) Oxidising agent
- (3) Reducing agent
- (4) Dehydrating agent
- 14. Sulphuric acid can be used as
  - (1) Hygroscopic agent
- (2) Oxidising agent
- (3) Sulphonating agent
- (4) Efflorescent
- 15. SF<sub>6</sub> and SF<sub>4</sub> involves hybridisation of the type and respectively.
  - $(1) sp^{3}$

(2)  $sp^3d$ 

 $(3) sp^3d^2$ 

- $(4) sp^2$
- **16.** Select the correct statements about  $Na_2S_2O_3 \cdot 5H_2O$ .
- (1) It is also called as hypo
- (2) It is used in photography to form complex with AgBr
- (3) It can be used as antichlor
- (4) It is used to remove stains of  $I_2$
- 17. Which of the following are amphoteric?
  - (1) BeO

(2) Al<sub>2</sub>O<sub>3</sub>

(3) ZnO

- (4) SO<sub>2</sub>
- **18.** In which of the following S—S link is present?
  - (1) Caro's acid
- (2) Dithionic acid
- (3) Thiosulphuric acid
- (4) Chlorosulphonic acid
- 19. A yellow coloured crystalline substance gave a colourless gas X on reaction with fluorine, which is thermally stable and has octahedral geometry. X can be
  - $(1) SF_{4}$

 $(3) SF_6$ 

 $(4) S_{2}F_{6}$ 

- 20. A green coloured solution of a salt changes its colour to light pink on passing ozone through it. Which of the following species represent pink and green colour respectively.
  - (1)  $Mn^{2+}$  and  $MnO_2$ (3)  $Co^{2+}$  and  $Co^{3+}$
- (2)  $MnO_4^{\Theta}$  and  $MnO_4^{2}$ (4)  $MnO_4^{2-}$  and  $MnO_4^{4}$   $\odot$
- 21. Which concentrated H<sub>2</sub>SO<sub>4</sub> can be used to dry the gas?
  - $(1) H_2S$

(3) NH<sub>3</sub>

- (4) All
- 22. Sulphur on reaction with concentrated HNO<sub>3</sub>. give<sub>8</sub> (A) which reacts with NaOH gives (B). (A) and (B) are
  - $(1) H_2SO_3, Na_2S_2O_3$
- (2) NO<sub>2</sub>, Na<sub>2</sub>S
- (3) H<sub>2</sub>SO<sub>4</sub>, Na<sub>2</sub>SO<sub>4</sub>
- $(4) H_2S_2O_3, Na_2S_2O_3$
- 23. The formation of which of the substance is known as tailing of mercury?
  - (1) Hg<sub>2</sub>O

- (2) HgO
- (3)  $Hg(NO_3)_2$
- (4) HgS
- 24. In which of the following species, S-atom assumes and hybrid state?
  - $I(SO_3); II(SO_2); III(H_2S); IV(S_8)$
  - (1) I, II

- (2) II, III
- (3) II, IV
- (4) III, IV
- 25. Which one of the following chemical reactions depicts the oxidising behaviour of H<sub>2</sub>SO<sub>4</sub>?
  - (1)  $2HI + H_2SO_4 \longrightarrow I_2 + SO_2 + 2H_2O$
  - (2)  $Ca(OH)_2 + H_2SO_4 \longrightarrow CaSO_4 + 2H_2O$
  - (3) NaCl +  $H_2SO_4 \longrightarrow NaHSO_4 + HCl$
  - (4)  $2PCl_5 + H_2SO_4 \longrightarrow 2POCl_3 + 2HCl + SO_2Cl_2$
- 26. Which of the following statements are true about sodium thisoulphate, Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>?
  - (1) It contains ionic, covalent and coordinate covalent bonds
  - (2) It is used to remove the unexposed AgBr from photographic films
  - (3) It can give a black precipitate with AgNO,
  - (4) It is used in the estimation of iodine
- 27. Which of the following statements are correct about halides of group-16 elements?
  - (1) All the elements form hexa-chlorides except oxygen and sulphur
  - (2) Order of thermal stability of the halides of any particular oxidation sate decreases in the order F > Cl > Br > I
  - (3) Te<sub>2</sub>Cl<sub>2</sub> and Po<sub>2</sub>Cl<sub>2</sub> are two well known compounds
  - (4) All the elements from hexafluoride except oxygen
- 28. Peroxy acids of sulphur are:
  - $(1) H_2 S_2 O_3$
- $(2) H_{2}S_{2}O_{7}$
- (3) H<sub>2</sub>SO<sub>5</sub>
- $(4) H_2 S_2 O_8$
- 29. Which of the following statements are correct about tetral halides?
  - (1) The tetra-halides are Lewis bases not Lewis acids
  - (2)  $SF_4 + 2H_2O \longrightarrow 4HF + SO_2$
  - (3)  $SF_6 + 3H_2O \longrightarrow 6HF + SO_3$
  - (4) TeCl<sub>4</sub> reacts with HCl to form complex ions such <sup>1</sup>  $[TeCl_6]^{2}$

30. Concentrated sulphuric acid is:

- (1) Sulphonating agent
- (2) Hygroscopic
- (3) Oxidizing agent
- (4) Efforescent
- 31. Select correct structures of oxyacid/oxide of sulphur.

$$(2) H_2S_2O_8 = \begin{cases} O & O \\ || & || \\ S & S \\ || & OH \\ OH & OH \end{cases}$$

$$(3) H_2S_4O_6 = HO S S S OH$$

- 32. The reaction of sodium thiosulphate with  $I_2$  gives:
  - (1) sodium tetrathionate
- (2) Sodium sulphate
- (3) Sodium iodide
- (4) Sodium sulphate
- 33. Sulphur dioxide can be used as:
  - (1) Bleaching agent
- (2) Disinfectant
- (3) Antichlor
- (4) None of these
- 34. In which of the following reactions conc. H<sub>2</sub>SO<sub>4</sub> is used as an oxidizing reagent?
  - $(1) NaCl + H<sub>2</sub>SO<sub>4</sub> \longrightarrow NaHSO<sub>4</sub> + HCl$
  - $(2) Cu + 2H<sub>2</sub>SO<sub>4</sub> \longrightarrow CuSO<sub>4</sub> + SO<sub>2</sub> + 2H<sub>2</sub>O$
  - $(3) 2HI + H<sub>2</sub>SO<sub>4</sub> \longrightarrow I<sub>2</sub> + SO<sub>2</sub> + 2H<sub>2</sub>O$
  - $(4) CaF<sub>2</sub> + H<sub>2</sub>SO<sub>4</sub> \longrightarrow CaSO<sub>4</sub> + 2HF$
- 35. Consider the following table:

Compound	Enthalpy of formation	Bond angle	Boiling
	$(kJ \text{ mol}^{-1})$	(H-C, A-H)	point (°C)
$H_2O$	$x_1$	$y_1$	$z_1$
$H_2S$	$x_2$	$y_2$	$z_2$
$H_2Se$	$x_3$	$y_3$	$z_3$
$H_2$ Te	$x_4$	$y_4$	$z_4$
According	to given information t	he correct order	· is/are:

cording to given information th

- $(1) x_1 > x_2 > x_3 > x_4$
- $(2)y_1 > y_2 > y_3 > y_4$
- $(3) z_1 > z_2 > z_3 > z_4$
- $(4) x_1 > x_4 > x_3 > x_2$
- 36. Which of the following orders represents the correct order for the properties indicated against them?
  - (1)  $H_2S < H_2Se < H_2Te$  (covalent character)
  - (2)  $H_2S > H_2Se > H_2Te$  (thermal stability)
  - (3)  $H_2S > H_2Se > H_2Te$  (reducing nature)
  - (4)  $H_2S < H_2Se < H_2Te$  (acidic character)
- 37. Which of the following statements are correct?
  - (1) Change in enthalpy is positive for the preparation of SO<sub>3</sub> by catalytic oxidation of SO<sub>2</sub>

- (2) Iron powder along with Al<sub>2</sub>O<sub>3</sub> and K<sub>2</sub>O is used as a catalyst in the preparation of NH<sub>3</sub> by Haber's process
- (3) In peroxosulphuric acid  $(H_2SO_5)$  sulphur is in oxidation
- (4) S-S bond is present in  $H_2S_2O_6$
- **38.** Select the correct statements.
  - (1)  $ZnO > Ga_2O_3 > Al_2O_3 > BeO$  (amphoteric oxides)
  - (2) Na2O behaves both as basic and as well as normal oxide
  - (3) Hg<sub>2</sub>O dissolves in Hg which loses its meniscus and stick to glass (tailing of mercury), is represented by the

- $O_3 + 2H^{\oplus} + 2H_{2(g)} \longrightarrow O_2 + H_2O + Hg_2^{2+}$ (4) During the oxidation of SnCl<sub>2</sub> to SnCl<sub>4</sub> by O<sub>3</sub>, O<sub>2</sub> is
- 39. Which of the following parent acid(s) does not have corresponding hypo-oxyacid?
  - $(1) HNO_3$
- (2) HClO<sub>3</sub>
- (3) H<sub>3</sub>PO<sub>4</sub>
- (4) H<sub>2</sub>SO<sub>4</sub>
- 40. Oxyanion (S) containing (6, 2) pair of equivalent X-O linkage (where X-central atom) is/are:
  - $(1) P_2 O_6^{4-}$
- $(3) P_{2}O_{7}^{4-}$
- **41.** Select the correct statement(s)
  - (1) NO and ClO<sub>2</sub> both have fractional bond order.
  - (2) NO and  $ClO_2$  both have odd  $e^-$  bond in their structures and both are paramagnetic.
  - (3) SF<sub>4</sub> is hydrolyzed by H<sub>2</sub>O to give H<sub>2</sub>SO<sub>3</sub> and HF as final
  - (4) During hydrolysis of SF<sub>4</sub>, S-atom in transition state is  $sp^3d^2$  hybridized.
- 42. What are the products in the following reaction?

$$S \stackrel{\circ}{+} \stackrel{\odot}{OH} \longrightarrow ?$$

 $(1) S^{2-}$ 

 $(3) S_5^{2-}$ 

- 43. Select the correct statement about  $O_3$ ?
  - (1)  $O_3$  oxidises  $[Fe(CN)_6]^{3-}$
  - (2) Moist I<sub>2</sub> reacts with O<sub>3</sub> to give I<sub>2</sub>O<sub>5</sub>
  - (3) O<sub>3</sub> acts as mild bleaching agent but cannot act as a bleaching agent in dry state
  - (4)  $O_3$  oxidies  $I^{\odot}$ , As $O_3^{3-}$  and Mn $O_4^{2-}$
- 44. Select the correct statements:
  - (1) Solid  $O_2$  is blue, liquid  $O_2$  is pale blue, and gaseous  $O_2$  is colourless.
  - (2) O<sub>2</sub> loses its paramagnetic character when it is cooled below a reaction temperature.
  - (3) O<sub>2</sub> does not react with, Zn, Ti and Fe directly.
  - (4) O<sub>3</sub> destroys mercury meniscus and is used in swimming pools.
- 45. Select the correct statements
  - (1) Monoclinic sulphur melts to clear mobile liquid at 119°C
  - (2) Monoclinic sulphur on heating from 160 to 190°C, it becomes viscous

- (3) Monoclinic sulphur on heating upto 200°C, the viscosity decreases
- (4) Dry SO<sub>2</sub> bleach dry flowers
- 46. Select the correct statements about the contact process for the manufacture of H<sub>2</sub>SO<sub>4</sub>
  - (1) Low temperature for the conversion of SO<sub>2</sub> to SO<sub>3</sub> is required, as the reaction is exothermic (720 K)
  - (2) High pressure (2 atm.) is required for the conversion of SO<sub>2</sub> to SO<sub>3</sub> which decreases in volume
  - (3) In contact process, SO<sub>3</sub> is not absorbed directly in H<sub>2</sub>O to form H<sub>2</sub>SO<sub>4</sub> because the reaction is highly exothermic, acid mist is formed. Hence the reaction becomes difficult to handle
  - (4) A catalyst (Pt or V<sub>2</sub>O<sub>5</sub>) is required to increase the yield of the reaction.

## **Linked Comprehension Type**

## Paragraph 1

H,SO<sub>4</sub> is the most important acid used in the chemical industry. Concentrated H<sub>2</sub>SO<sub>4</sub> has quite strong oxidising properties.

- 1. H<sub>2</sub>SO<sub>4</sub> acts as
  - (1) Reducing agent
- (2) Oxidising agent
- (3) Only monobasic acid
- (4) None of these
- 2. The shape of  $H_2SO_4$  is
  - (1) Tetrahedral
- (2) Pyramidal
- (3) Planar
- (4) T-shaped
- 3. Oxidation state of S in H<sub>2</sub>SO<sub>4</sub> is
  - (1) +6

(2) +4

(3) + 2

(4) + 3

#### Paragraph 2

Hydrogen peroxide is an important compound of hydrogen and oxygen. It shows various types of properties and chemical reactions.

- 4. Hydrogen peroxide is not
  - (1) A reducing agent
- (2) An oxidising agent
- (3) A dehydrating agent
- (4) A bleaching agent
- 5. The reaction  $H_2S + H_2O_2 \longrightarrow S + 2H_2O$  manifests
  - (1) Acidic nature of H<sub>2</sub>O<sub>2</sub>
- (2) Alkaline nature of H<sub>2</sub>O<sub>2</sub>
- (3) Oxidising action of H<sub>2</sub>O<sub>2</sub> (4) Reducing nature of H<sub>2</sub>O<sub>2</sub>
- 6. The species that do not contain peroxide ion (s) is/are
  - (1) PbO<sub>2</sub>

- (2) SrO<sub>2</sub>
- (3) Na<sub>2</sub>O<sub>2</sub>
- (4) BaO<sub>2</sub>
- 7. The oxidation state of oxygen in  $H_2O_2$  is
  - (1) + 1

(2)-1

(3) + 2

(4) - 2

## Paragraph 3

Sulphuric acid is considered as the king of chemicals. The prosperity of any country is measured by the amount of sulphuric acid it consumes. Sulphuric acid is, thus, a substance of very great commercial importance as it is used practically in every important industry. This is due to the following properties of sulphuric acid:

- (1) acidic nature
- (2) oxidising nature
- (3) dehydrating nature
- (4) sulphonation
- 8. Sulphuric acid has very corrosive action on skin because
  - (1) It reacts with proteins
  - (2) It acts as an oxidising agent
  - (3) It acts as a dehydrating agent
  - (4) It acts as a dehydrating agent and absorption of water is highly exothermic
- 9. Which of the following reactions depict the  $oxidisin_0$ behaviour of H<sub>2</sub>SO<sub>4</sub>?
  - (1)  $2HI + H_2SO_4 \longrightarrow I_2 + SO_2 + 2H_2O$
  - (2)  $NaCl + H_2SO_4 \longrightarrow NaHSO_4 + HCl$
  - (3)  $2\text{NaOH} + \text{H}_2\text{SO}_4 \longrightarrow \text{Na}_2\text{SO}_4 + 2\text{H}_2\text{O}$
  - (4)  $2PCl_5 + H_2SO_4 \longrightarrow 2POCl_3 + 2HCl + SO_2Cl_2$
- 10. Sulphuric acid is used
  - (1) In lead storage batteries (2) In making fertilizers
  - (3) In making explosives
- (4) All of these
- 11. Concentrated  $\rm H_2SO_4$  cannot be used to prepare  $\rm HB_{I\ or\ HI}$ from KBr or KI because it
  - (1) Reacts too slowly with KBr or KI
  - (2) Reduces HBr or HI
  - (3) Oxidises HBr or HI
  - (4) Oxidises KBr to KBrO<sub>3</sub> or KI to KIO<sub>3</sub>
- 12. Only carbon is obtained when concentrated  $H_2SO_4$  is added
  - (1) Formic acid
- (2) Cane sugar
- (3) Oxalic acid
- (4) Ethyl alcohol
- 13. The formation of nitroglycerine is done by the use of concentrated nitric acid and concentrated sulphuric acid The process of conversion of glycerine into nitroglycerine is termed as
  - (1) Sulphonation
- (2) Oxidation
- (3) Nitration
- (4) Dehydration

## Paragraph 4

The binary compounds of oxygen with other elements are called oxides. They are classified depending either upon their acid-base characteristics or on the basis of oxygen content.

- (1) Normal oxides: These oxides which contain oxygen atoms as permitted by the normal oxidation number, i.e., -2 normal oxide may be acidic, basic, amphoteric or neutral
- (2) Polyoxides: The oxides which contain oxygen atoms different than those permitted by the normal oxidation number of -2.
  - i. Peroxides: Two oxygen atoms are linked to each other and each oxygen has -1 oxidation number. They contain  $(O - O)^{2-}$  unit.
  - ii. Superoxides: These oxides contain  $(O-O)^{-1}$  unit, i.e., each O-atom has oxidation number -1/2.
- (3) Suboxides: These contain low content of oxygen than expected.
- (4) Mixed oxides: These oxides are made of two simpler oxides.

- 14. Which pair of species is referred to as suboxides?
  - (1) CO, NO
- (2) SO<sub>2</sub>, CaO
- $(3) N_2O, CO$
- (4) N<sub>2</sub>O, C<sub>3</sub>O<sub>2</sub>
- 15. Which of the following pairs contains neutral oxides?
  - $(1) SO_2, SO_3$
- $(2) N_2 O_3, N_2 O_5$
- (3) CO, NO
- (4) Na<sub>2</sub>O, CaO
- 16. Which of the following pairs contains mixed oxides?
  - (1) Pb<sub>3</sub>O<sub>4</sub>, Fe<sub>3</sub>O<sub>4</sub>
- (2) MnO<sub>2</sub>, BaO<sub>2</sub>
- (3) KO<sub>2</sub>, Na<sub>2</sub>O<sub>2</sub>
- (4) Mn<sub>3</sub>O<sub>4</sub>, N<sub>2</sub>O<sub>5</sub>
- 17. Which of the following pairs contains amphoteric oxides?
  - (1) BeO, BaO
- (2) BeO,  $Al_2O_3$
- $(3) Al_2O_3, P_2O_5$
- (4) FeO, CuO
- 18. Which of the following oxides is paramagnetic in nature?
  - (1) KO,

(2) BaO<sub>2</sub>

 $(3) H_2O$ 

(4) CO<sub>2</sub>

## paragraph 5

Sulphur and rest of the elements of group 16 are less electronegative than oxygen. Therefore, their atoms cannot take electrons easily. They can acquire  $ns^2np^6$  configuration by sharing two electrons with the atoms of other elements and thus, exhibit +2 oxidation state in their compounds. In addition to this, their atoms have vacant d-orbitals in their valence shell to which electrons can be promoted from the p and s-orbitals of the same shell. As a result, they can show +4 and +6 oxidation states.

- 19. The oxidation state of sulphur in  $S_8$ ,  $SO_3$  and  $H_2S$  respectively
  - (1) 0, +6, -2
- (2) +2, +6, -2
- (3) 0, +4 +2
- (4) -2, +6, +2
- 20. The oxidation state of sulphur in  $Na_2S_4O_6$  is
  - (1) 2/3

(2) 3/2

(3) 3/5

- (4) 5/2
- 21. The nature of the compounds of sulphur having +4 oxidation
  - (1) Act as oxidising agents
    - (2) Act as reducing agents
    - (3) Act as oxidising as well as reducing agents
    - (4) Cannot be predicted
- 22. Like sulphur, oxygen does not show +4 and +6 oxidation states. The reason is
  - (1) That oxygen is a gas while sulphur is a solid
  - (2) That oxygen has high ionisation enthalpies in comparison to sulphur
  - (3) That oxygen has high electron affinity in comparison to sulphur
  - (4) That oxygen has no d-orbitals in its valence shell
- 23. Oxygen exhibits +2 oxidation state in
  - $(1) H_2O$

- (2) OF,
- (3) Cl<sub>2</sub>O

 $(4) H_2O_2$ 

## **Matching Column Type**



This section contains questions each with two columns I and II. Match the items given in column I with that in column II.

	Column I		Column II		
a.	SOF <sub>2</sub>	p.	Oxyacid formed during hydrolysis undergo tautomeric change		
b.	H <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	q.	Oxidation state of central atom does not change during hydrolysis		
c.	XeOF <sub>4</sub> r	XeOF <sub>4</sub> r.	XeOF <sub>4</sub> r. Both partial and		Both partial and complete hydrolysis is possible
d.	POCl <sub>3</sub>	s.	Hydrolyzed product reacts with glass		
		t.	Hybridization of central atom in the final product-remains same as in the substrate on hydrolysis		

Column I		Column II			
a.	$H_2S_2O_8 \xrightarrow{H_2O}$	p.	Dibasic acid		
b.	$SF_4 \xrightarrow{H_2O}$	q.	Can act as flexidentate ligand		
c.	$NCl_3 \xrightarrow{H_2O}$	r.	Can act as both oxidizing and reducing agent		
d.	$NO_2 \xrightarrow{H_2O}$	s.	Can act as mono-dentate ligand		
		t.	Non-redox hydrolysis		

<b>3.</b>		Column I (Property of SO <sub>2</sub> )		Column II (Reaction)	
	a.	Acidic nature	p.	$2Mg + SO_2 \rightarrow 2MgO + S$	
	b.	Oxidising nature	q.	$CaO + SO_2 \rightarrow CaSO_3$	
	c.	Reducing nature	r.	$2H_2S + SO_2 \rightarrow 3S + 2H_2O$	
	d.	Non-supporter of combustion	s.	$Cr_2O_7^{2-} + 2H^{\oplus} + 3SO_2$ $\rightarrow 3SO_4^{2-} + H_2O + 2Cr^{3+}$	

	Column I		Column II
a.	<ul><li>a. Oil of vitriol</li><li>b. Fuming H<sub>2</sub>SO<sub>4</sub></li></ul>		$H_2S_2O_7$
b.			H <sub>2</sub> SO <sub>5</sub>
c.	Oleum	r.	H <sub>2</sub> SO <sub>4</sub>
d.	Caro's acid	s.	$SO_3 + H_2SO_4$

5.		Column I (Compound of S)	Column II (Hybridisation of S)			
	a.	SF <sub>6</sub>	i.	$sp^3d$		
	b.	SO <sub>2</sub>	ii.	$sp^3$		
	c.	SCl <sub>4</sub>	iii.	$sp^2$		
	d.	H <sub>2</sub> SO <sub>4</sub>	iv.	$sp^3d^2$		

6.		Column I (Allotropic form)	Column II (Structure)			
	a.	Engel's sulphur	p.	Rings, chair conformation, stable		
	b.	Sulphur	q.	Fibrous or rubber like		

Rhombic sulphur		Crystalline form, yellow crystals
Monoclinic sulphur	S.	Puckered S <sub>8</sub> rings, crown conformation
		Manaclinic sulphur S.

7. Match the items given in Column I with that in Column II and III.

	Column I		Column II		Column III
	Oxides		Compounds		Characteristics
a.	Superoxides	i.	C <sub>3</sub> O <sub>2</sub>	p.	React with water to give H <sub>2</sub> O <sub>2</sub> and O <sub>2</sub>
b.	Peroxides	ii.	CsO <sub>2</sub>	q.	React with dil. H <sub>2</sub> SO <sub>4</sub> to give H <sub>2</sub> O <sub>2</sub> and with conc. H <sub>2</sub> SO <sub>4</sub> to give H <sub>2</sub> O <sub>2</sub> +
c.	Suboxides	iii.	N <sub>2</sub> O	r.	Contains 3ē bonds and are paramagnetic and coloured
d.	Neutral oxide	iv.	BaO <sub>2</sub>	s.	They involve M–M bonds in addition to M–O bonds

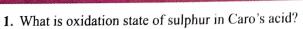
8. Match the items given in Column I with that in Column II and III.

Mat	ch the items given in Column I with that in		Column II		Column III
Column I			Characteristics (II)		Compound
	Characteristics (I)		Characteristics (11)	p.	0,
a.	In Solid State it exists as a cyclic trimer or a linear polymeric chain structure.	i.	Element is used for photocopying (Xerox). It is also used as a decolouriser of glass	P.	2
b.	In solid state it exists as cyclic tetramer structure	ii.	Trigangular plannar gaseous molecule at room temperature. $sp^2$ hybridised, with 2 $(p\pi - d\pi)$ bond	q.	SeO <sub>3</sub>
c.	Pale blue gas and is diamagnetic	iii.	Used in Ostwall process	r.	SO <sub>3</sub>
d.	It oxidises NH <sub>3</sub> to NO(g) in presence of Pt gauge as catalyst at 1100 K	iv.	The gas reacts with Hg and Hg <sub>2</sub> O is formed which dissolves in Hg, which loses its meniscus and sticks to glass. It is called tailing of mercury	s.	O <sub>3</sub>

9. Match the items given in Column I with that in Column II and III.

Column I			Column II		Column III
14	Oxo-acids of phosphorous		Characteristics (I)		Characteristics (II)
a.	Phosphinic acid	i.	Dibasic, (+3) O.S., 2(P–OH), 1(P–H), and 1(P=0) bond	p.	$P_4 + 3NaOH \longrightarrow PH_3 + 3H_2O + \dots$
b.	Phosphonic acid	ii.	Tribasic, (+5) O.S. 2(P–OH), 1(P=0) and 1(P–0–O–H) bond	q.	$2H_3PO_4 \xrightarrow{520 \text{ K}} H_4P_2O_7 \xrightarrow{870 \text{ K}} \dots$
c.	Metaphosphoric acid	iii.	Monobasic, (+1) O.S. 1(P–OH), 2(P–H) and 1(P=0) bond	r.	PCl <sub>3</sub> + 3H <sub>2</sub> O → 3HCl +
d.	Per mono-oxo-phosphoric acid	iv.	Monobasic (+5) O.S. 1(P–OH) and 2(P=0) bond. Exists in polymeric form	S.	$P_4O_{10} + 4H_2O_2 (30\%) + 2H_2O \longrightarrow$
				t.o	Strongest reducing agent

## Numerical Value Type



- 2. How many  $\pi$ -bonds are present in Marshall's acid?
- 3. Ozone reacts with dry iodine to form an oxide having oxygen atoms in its molecules.
- 4. How many S-S bonds are present in  $S_8$  molecule?
- **5.** Among the oxides given below, how many are acidic? CrO<sub>3</sub>, Mn<sub>2</sub>O<sub>7</sub>, CuO, CO, SO<sub>2</sub>

**6.** In how many of the following species, S-atom is \$\foats\$ hybridised?

S<sub>8</sub>, SO<sub>4</sub><sup>2-</sup>, SO<sub>3</sub>, H<sub>2</sub>S, SCl<sub>4</sub>

- 7. What is the number of σ bonds present in peroxodisulphuracid?
- 8. Conc. H<sub>2</sub>SO<sub>4</sub> reacts with four moles of Ag to give \_\_\_\_ moles of Ag<sub>2</sub>SO<sub>4</sub>.
- 9. If P represent total number of lone pairs (non bonding electron pairs)

Q represent total number of  $\pi$ -bonds.  $\frac{z}{R}$  represents total number of  $\sigma$ -bonds

Then calculate the value (P + Q - R) in pentathionic acid.

P, Q and R are total number of  $(p\pi - d\pi)$  bonds in (i)  $H_2S_2O_5$  (ii)  $H_2S_2O_6$  and (iii)  $H_2SO_3$  then calculate the value of (P+Q+R).

11. If P represents  $sp^3$ -hybridised atoms

O represents  $sp^2$ -hybridised atoms.

R represents number of  $(p\pi - d\pi)$  bonds.

Then calculate the value of (P + R - Q) in Marshall's acid.



## **Archives**



## JEE MAIN

## Single Correct Answer Type

- 1. Which of the following statements regarding sulphur is incorrect?
  - (1) S, molecule is paramagnetic
  - (2) The vapor at 200°C consists mostly of S<sub>8</sub> rings
- (3) At 600°C, the gas mainly consists of S<sub>2</sub> molecules
- (4) The oxidation state of sulphur is never less than +4 in its compounds (AIEEE 2011)
- 2. The products obtained on heating LiNO, will be
  - (1) LiNO<sub>2</sub> + O<sub>2</sub>
- $(2) \text{Li}_2 \text{O} + \text{NO}_2 + \text{O}_2$
- (3)  $\text{Li}_3 N + O_2$
- $(4) \text{Li}_2 \text{O} + \text{OH} + \text{O}_2$

(AIEEE 2011)

- 3. Which of the following is wrong statement?
  - (1) ONCl and ONO are not isoelectronic
  - (2) O<sub>3</sub> molecule is linear
  - (3) Ozone is violet-black in solid sate
  - (4) Ozone is diamagnetic gas

(JEE Main 2013)

#### JEE ADVANCED

## Single Correct Answer Type

- 1. The number of S—S bonds in sulphur trioxide trimer  $(S_3O_9)$ is
  - (1) three

(2) two

(3) one

(4) zero

(IIT-JEE 2001)

- 2. Which of the following is not oxidised by  $O_3$ ?
  - (1) KI

- (2)  $FeSO_4$
- $(3) \text{ KMnO}_{4}$
- $(4) K_2 MnO_4$

(IIT-JEE 2005)

- 3. The species having pyramidal shape is
  - (1) SO<sub>3</sub>

- (2) BrF<sub>3</sub>
- (3)  $SiO_3^{2-}$

(4) OSF<sub>2</sub>

(IIT-JEE 2010)

- 4. Which of the following does not give oxygen on heating?
  - (1) K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>
- $(2) (NH_4)_2 Cr_2 O_7$
- (3) KClO<sub>3</sub>
- (4)  $Zn(ClO_3)_2$

(JEE Advanced 2013)

## **Multiple Correct Answers Type**

- 1. The pair(s) of reagents that yield paramagnetic species
  - (1) Na and excess of NH<sub>3</sub>
- (2) K and excess of  $O_2$
- (3) Cu and dilute HNO<sub>3</sub>
- (4) O2 and 2-ethylanthraquinol

(JEE Advanced 2014)

## **Numerical Value Type**

- 1. Among the following, how many elements show only one non-zero oxidation state?
  - O, Cl, F, N, P, Sn, Tl, Na, Ti

(IIT-JEE 2010)

2. The value of n in the molecular formula  $Be_nAl_2Si_6O_{18}$  is

(IIT-JEE 2010)

3. Amongst the following, the total number of compounds whose aqueous solution turns red litmus paper blue.

KCN, K<sub>2</sub>SO<sub>4</sub>, (NH<sub>4</sub>)<sub>2</sub>C<sub>2</sub>O<sub>4</sub>, NaCl Zn(NO<sub>3</sub>)<sub>2</sub>, FeCl<sub>3</sub>, K<sub>2</sub>CO<sub>3</sub>, NH<sub>4</sub>NO<sub>3</sub>, LiCN.

(IIT-JEE 2010)

4. The difference in the oxidation number of two types of S-atoms in  $Na_2S_4O_6$  is

(IIT-JEE 2011)

5. A list of species having the formula  $XZ_4$  is given below:

 $XeF_4$ ,  $SF_4$ ,  $SiF_4$ ,  $BF_4^{\Theta}$ ,  $[Cu(NH_3)_4]^{2+}$ ,  $[FeCl_4]^{2-}$ ,  $[CoCl_4]^{2-}$ and  $[PtCl_{4}]^{2-}$ .

Defining shape on the basis of the location of X and Z atoms, the total number of species having a square planar shape is

(JEE Advanced 2014)

## **Answers Key**

#### **EXERCISES**

### **Single Correct Answer Type**

1.(2)	<b>2.</b> (1)	3. (4)	<b>4.</b> (2)	<b>5.</b> (4)
6. (4)	7.(3)	8. (3)	<b>9.</b> (3)	<b>10.</b> (2)
11.(2)	<b>12.</b> (3)	13. (4)	14. (4)	<b>15.</b> (3)
16. (3)	<b>17.</b> (1)	<b>18.</b> (3)	<b>19.</b> (1)	<b>20.</b> (1)
21.(1)	22.(3)	23. (2)	<b>24.</b> (2)	<b>25.</b> (3)
26. (4)	27.(1)	28. (2)	<b>29.</b> (1)	<b>30.</b> (4)
31.(2)	32.(4)	33. (1)	34. (2)	<b>35.</b> (3)
36.(2)	37.(2)	38. (3)	<b>39.</b> (4)	<b>40.</b> (2)
41.(1)	42.(1)	43. (2)	<b>44.</b> (3)	<b>45.</b> (4)
46.(1)	47. (4)	48. (2)	<b>49.</b> (4)	<b>50.</b> (1)
51.(2)	<b>52.</b> (3)	<b>53.</b> (3)	<b>54.</b> (2)	<b>55.</b> (3)
56. (4)	<b>57.</b> (1)	<b>58.</b> (4)	<b>59.</b> (2)	<b>60.</b> (1)
61.(2)	<b>62.</b> (3)	<b>63.</b> (3)	<b>64.</b> (1)	<b>65.</b> (2)
66. (3)	<b>67.</b> (2)	<b>68.</b> (3)	<b>69.</b> (4)	<b>70.</b> (1)
71.(3)	<b>72.</b> (1)	<b>73.</b> (1)	<b>74.</b> (1)	<b>75.</b> (4)
76. (3)	<b>77.</b> (3)			

### **Multiple Correct Answers Type**

•		
<b>1.</b> (1, 2, 3)	<b>2.</b> (1, 3)	<b>3.</b> (1, 2, 4)
4. (1, 2)	<b>5.</b> (3)	<b>6.</b> (1, 3, 4)
<b>7.</b> (1, 2, 4)	<b>8.</b> (1, 2, 3)	<b>9.</b> (2, 3, 4)
<b>10.</b> (3, 4)	<b>11.</b> (2, 4)	<b>12.</b> (2, 3)
<b>13.</b> (1, 2, 3)	<b>14.</b> (1, 2, 3)	<b>15.</b> (2, 3)
<b>16.</b> (1, 2, 3, 4)	<b>17.</b> (1, 2, 3)	<b>18.</b> (2, 3)
<b>19.</b> (3)	<b>20.</b> (4)	<b>21.</b> (2)
<b>22.</b> (3)	<b>23.</b> (1)	<b>24.</b> (4)
<b>25.</b> (1)	<b>26.</b> (2, 3, 4)	<b>27.</b> (1)
<b>28.</b> (2, 4)	<b>29.</b> (1, 4)	<b>30.</b> (1, 2, 3)
<b>31.</b> (1, 3, 4)	<b>32.</b> (1, 3)	<b>33.</b> (1, 2, 3)
<b>34.</b> (2, 3)	<b>35.</b> (1, 2, 3)	<b>36.</b> (1, 2, 4)
<b>37.</b> (3, 4)	<b>38.</b> (2, 3)	<b>39.</b> (1, 2)
<b>40.</b> (2, 3, 4)	<b>41.</b> (1, 2, 3, 4)	<b>42.</b> (1, 3, 4)
<b>13.</b> (3, 4)	<b>44.</b> (1, 2, 4)	<b>45.</b> (1, 2, 3)
<b>6.</b> (1, 2, 3)		(1, 2, 3)

## **Linked Comprehension Type**

<b>1.</b> (2)	<b>2.</b> (1)	<b>3.</b> (1)	<b>4.</b> (3)	<b>5.</b> (1)
<b>6.</b> (1)	<b>7.</b> (2)	<b>8.</b> (4)	<b>9.</b> (1)	10. (4)

11. (3)	<b>12.</b> (2)	<b>13.</b> (3)	<b>14.</b> (4)	<b>15.</b> (3)
<b>16.</b> (1)	<b>17.</b> (2)	<b>18.</b> (1)	<b>19.</b> (1)	<b>20.</b> (4)
21. (3)	<b>22.</b> (4)	<b>23.</b> (2)		()

## **Matching Column Type**

Q.No.	a.	b.	c.	d.
1.	q	r	S	р
2.	S	r	q	р
3.	q	r	S	р
4.	r	S	p	q
5.	S	r	p	q
6.	р	S	r	q
7.	ii–p,r	iv-q	i, iii–s	iii—s
8.	ii–r	i–q	iv-s	iii–p
9.	iii–p,t	i–r	iv–q	ii–s

#### **Numerical Value Type**

1. (6)	<b>2.</b> (4)	<b>3.</b> (9)	<b>4.</b> (8)	<b>5.</b> (3)
<b>6.</b> (3)	<b>7.</b> (9)	<b>8.</b> (2)	<b>9.</b> (10)	<b>10.</b> (8)

## **11.** (1.2)

## ARCHIVES JEE Main

## Single Correct Answer Type

1. (4)	<b>2.</b> (2)	<b>3.</b> (2)
( .)	<b></b> (-)	3. (2)

#### JEE Advanced

### **Single Correct Answer Type**

1. (4)	<b>2.</b> (3)	3. (4)	<b>4.</b> (2)
	(-)	2. (1)	7. (2

## **Multiple Correct Answers Type**

1. (1, 2, 3)

## **Numerical Value Type**

1. (2)	<b>2.</b> (3)	<b>3.</b> (3)	4. (5)	<b>5.</b> (4)



## p-Block **Group 17 Elements** The Halogen Family

## **OVERVIEW**

- 1. Group 17 of the periodic table consists of fluorine (F), chlorine (Cl), bromine (Br), iodine (I) and astatine (At). Collectively, these elements are also known as halogens (Greek: 'halo' meaning 'salt' and 'genes' meaning 'born' or 'salt producer').
- 2. General electronic configuration of halogens is  $ns^2np^5$ , i.e. they are just short of one electron to attain the stable electronic configuration of the next noble gas.
- 3. Due to their high reactivity, halogens are never found in free state, but in the combined state. Fluorine is known as 'super halogen'.
- 4. All halogens exist as diatomic molecules, X<sub>2</sub>. At room temperature, F<sub>2</sub> and Cl<sub>2</sub> are gases, Br<sub>2</sub> is liquid and I<sub>2</sub> is solid. Weak van der Waals forces of attraction hold the diatomic molecules together, and as these forces increase with molecular mass, nature of halogens changes from gas  $\longrightarrow$  liquid  $\longrightarrow$  solid.
- 5. i. Atomic radii: F < Cl < Br < I
  - ii. Melting point:  $F_2 < Cl_2 < Br_2 < I_2$
  - iii. Boiling point:  $F_2 < Cl_2 < Br_2 < I_2$
- 6. Halogens have high ionisation enthalpies. Ionisation enthalpy: F < Cl < Br < I.

Iodine forms positive ion,  $I^{\oplus}$ , i.e. shows metallic character, non-metallic character decreases from F to I.

- 7. All the halogens are coloured, due to absorption of some wavelength of visible light by their molecules to cause
  - $\pi^* \longrightarrow \sigma^*$  transition.

 $Br_2$ 

 $I_2$ 

Yellowish green Greenish yellow Brownish red

**8.** Electronegativity: F > Cl > Br > I

Fluorine is the highest electronegative element of the periodic table.

**9.** Electron affinity: F < Cl > Br > I

F has less electron affinity than Cl due to high repulsion between the electron to be added and the electrons already present in F (due to small size of F).

**10.** Bond length:  $F_2 < Cl_2 < Br_2 < I_2$ 

Despite the fact that bond length of  $F_2 < Cl_2$ , bond dissociation enthalpy of F<sub>2</sub> is less than Cl<sub>2</sub>. This is due to high lp—lp repulsion between the electrons present in F—F.

11. Fluorine shows an oxidation state of -1 only, except in HOF, where its oxidation state is +1.

Cl, Br and I show -1, +1, +3, +5 and +7 oxidation states. Due to presence of vacant d-orbitals in Cl, Br and I, higher oxidation states are possible. In oxides and oxyacids, +4 and +6 oxidation states are also shown.

12. Standard reductive potentials of halogens are positive and decrease from F to I. Thus halogens act as strong oxidising

- Oxidising power: F<sub>2</sub> > Cl<sub>2</sub> > Br<sub>2</sub> > I<sub>2</sub>
  13. F<sup>⊖</sup> ion does not show any reducing nature, but Cl<sup>⊖</sup>, Br<sup>⊖</sup> and I<sup>⊖</sup> act as reducing agent.
- 14. With water: Fluorine reacts with water even in dark, producing  $O_2$  and  $O_3$ .

$$2F_2 + 2H_2O \longrightarrow 4HF + O_2$$

$$3F_2 + 3H_2O \longrightarrow 6HF + O_3$$

Cl<sub>2</sub> and Br<sub>2</sub> are fairly soluble in water and form chlorine water and bromine water. I<sub>2</sub> does not dissolve in water. I<sub>3</sub> is more soluble in KI solution than in pure water, due to formation of polyhalide,  $I_3^{\odot}$  ion.

$$I_2 + I^{\bigcirc} \rightleftharpoons I^{\bigcirc}_{3(aq)}$$

On careful evaporation of Cl<sub>2</sub> water or Br<sub>2</sub> water, crystals of composition Cl<sub>2</sub>·8H<sub>2</sub>O and Br<sub>2</sub>·8H<sub>2</sub>O are formed.

- 15. Aqueous solution I<sub>2</sub> is brown in colour while organic solutions of I<sub>2</sub> are violet in colour.
- 16. I<sub>2</sub> is used in medicine in the form of tincture of iodine (2-3% alcoholic solution of  $I_2$ ) and iodex ointment (consists of I<sub>2</sub> and methyl salicylate in a vaseline base).
- 17. NaBr and KBr are used as sedatives.
- 18. With hydrogen, all the halogens form volatile covalent hydrides, HX. These hydrides are known as halogen acids or hydracids.

HF is a liquid due to association of molecules through hydrogen bonding.

**Boiling** point : HF > HCl > HBr > HI

Bond strength : HF > HCl > HBr > HI

iii. Bond dissociation enthalpy: HF > HCl > HBr > HI

: HF < HCl < HBr < HI iv. Reducing nature

(HF does not show reducing nature)

: HF > HCl > HBr > HI Dipole moment  $(\mu)$ 

19. Halogens and oxygen do not combine directly with each other. However, these compounds have been obtained indirectly. The known compounds are:

$OF_2$	Cl <sub>2</sub> O	$\mathrm{Br_2O}$	$I_2O_5$
$O_2F_2$	$ClO_2$	$BrO_2$	
	$\text{Cl}_2\text{O}_6$	$BrO_3$	
	$\text{Cl}_2\text{O}_7$		

The compounds of oxygen and fluorine are not called oxides but fluorides as fluorine is more electronegative than oxygen.

- Oxides of Cl, Br and I are acidic and acidic character increases with increase of percentage of oxygen in them.
- ii. All the oxides of halogens are powerful oxidants, highly reactive and unstable towards heat. In general, higher oxides are relatively more stable than lower oxides for a particular halogen.
- iii. Oxygen fluorides do not form oxyacids.
- iv. In these oxides, bonds are mainly covalent due to small difference in the electronegativity of oxygen and
- v. All the three monoxides, viz., OF<sub>2</sub>, Cl<sub>2</sub>O and Br<sub>2</sub>O have tetrahedral geometry involving sp<sup>3</sup> hybridisation of oxygen, bond angle increases with increase in size of the halogen atom.
- vi. Oxides of iodine  $I_2O_4$  and  $I_4O_9$  are not true oxides but iodates, IO(IO<sub>3</sub>) and I(IO<sub>3</sub>)<sub>3</sub> respectively.
- 20. Except fluorine, all other halogens form oxyacids of the type HOX, HXO<sub>2</sub>, HXO<sub>3</sub> and HXO<sub>4</sub>. Some of these acids are quite unstable.

cl Cl	Br	I	
HOCl	HOBr	HOI	Hypohalous
HClO <sub>2</sub>		_	Halous
HClO <sub>3</sub>	$\mathrm{HBrO}_3$	$HIO_3$	Halic
HClO <sub>4</sub>	$\mathrm{HBrO}_4$	$HIO_4$	Perhalic

- i. All these acids are monobasic and the halogen atom is sp<sup>3</sup> hybridised.
- ii. Acidic character increases with increase in oxidation number of the halogen.

$$\mathrm{HOCl} < \mathrm{HClO}_2 < \mathrm{HClO}_3 < \mathrm{HClO}_4$$

iii. In any series, acidic character decreases as the electronegativity decreases.

$$HCIO_4 > HBrO_4 > HIO_4$$

iv. Oxidising nature for the same halogen decreases.

$$HOCl > HClO_2 > HClO_3 > HClO_4$$

v. Stability for the same halogen increases. HOCl < HClO<sub>2</sub> < HClO<sub>3</sub> < HClO<sub>4</sub>

- 21. The important minerals of fluorine are:
  - (i) Fluorspar (CaF<sub>2</sub>); (ii) Cryolite (Na<sub>3</sub>AlF<sub>6</sub>);
  - (iii) Fluorapatite [CaF<sub>2</sub>·3Ca<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>]

In small amounts, it is present as fluorides in plant ashes, soil, sea water, bones and teeth of animals.

Fluorine was discovered by Joseph Henri Moissan in 1886.

- 22. The fluorine compounds have wide applications:
  - a. Freon, CF<sub>2</sub>Cl<sub>2</sub> (dichlorodifluoro methane) is used in refrigerants and cold storage plants.

- b. Teflon (C<sub>2</sub>F<sub>4</sub>), a new plastic, has a very high electrical resistance and is used as insulating material. It is not resistance and is used as insulating material. It is not resistance and is used as insulating material. affected by acids, alkalies and strong oxidising agents
- c. H<sub>2</sub>F<sub>2</sub> is used for etching of glass.
- **d.** SF<sub>6</sub> has insulating properties. It is used in X-ray  $a_{hd}$ high voltage machines.
- e. NaF and Na<sub>3</sub>AlF<sub>6</sub> are used as insecticides.
- CuF<sub>2</sub> is used in ceramic industry.
- $UF_6$  is used for separation of <sup>235</sup>U isotope from natural
- h. Sodium fluoroacetate is used as a rat poison.
- 23. Chlorine was discovered by Scheele in 1774. The old name is oxymuriatic acid gas. Common salt (NaCl) is the most important chloride which occurs in sea water, lakes and in rocks.
- 24. Chlorine is a yellowish green gas with pungent suffocation and poisonous nature. It is fairly soluble in water. The aqueous solution is called chlorine water which gives crystal of chlorine hydrate (Cl<sub>2</sub>·8H<sub>2</sub>O) at 0°C. In presence of moisture it acts as an oxidising and bleaching agent,
- 25. Chlorine is used in the manufacture of bleaching powder, chlorates, hypochlorites, HCl, chloroform, CCl phosgene (COCl<sub>2</sub>), tear gas (CCl<sub>3</sub>NO<sub>2</sub>) and mustard gas (Cl-C<sub>2</sub>H<sub>4</sub>-S-C<sub>2</sub>H<sub>4</sub>-Cl). It is used in the purification of drinking water and as a bleaching agent for cotton fabrics paper and rayon.
- 26. Bromine was discovered by Balard in 1826. It is obtained either from the mother liquor (called bittern) obtained after crystallising KCl from carnallite or from sea water by passing Cl<sub>2</sub> gas. The vapours are absorbed in Na,CO, solution when a mixture of NaBr and NaBrO<sub>3</sub> is obtained which is distilled with H<sub>2</sub>SO<sub>4</sub> to recover bromine.
- 27. Iodine was discovered by Courtois in 1812. Two main sources of iodine are:
  - Deep sea-weeds ashes known as kelp which contains 0.5% iodine in the form of iodides.
  - **b.** Caliche or crude chile saltpetre which contains 0.2% of NaIO<sub>3</sub>.
- 28. I<sub>2</sub> is slightly soluble in water. The solubility can be increased by addition of KI.

$$KI + I_2 \longrightarrow KI_3$$
 (Soluble)

It is soluble in organic solvents such as chloroform, carbon tetrachloride, alcohol, ether, etc. It oxidises Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> into sodium tetrathionate. This reaction is useful in iodometro titrations.

29. The halogens on account of difference in the electronegativities combine with each other to form compounds of the type AX, where A is always a bigger atom and X is a smaller atom and n may have values 1, 3, 5 and 7. These are covalent compounds called interhalogen compounds AX type ClF, BrF, BrCl, ICl, IBr  $\longrightarrow sp^3d$  hybridisation

of A, three lone pairs

 $AX_3$  type  $ClF_3$ ,  $BrF_3$ ,  $ICl_3 \longrightarrow sp^3d$  hybridisation of A, two lone pairs.

 $AX_5$  type IF<sub>5</sub>,  $BrF_5 \longrightarrow sp^3d^2$  hybridisation of A, one lone pair.  $AX_7$  type IF<sub>7</sub>  $\longrightarrow sp^3d^3$  hybridisation of A.

Interhalogen compounds are gases or liquids. These are volatile and fume in air. These compounds are more reactive than halogens except fluorine because A—B bond is weaker than A—A and B—B bond. These are hydrolysed and act as oxidising agents.

10. Halide ions often react with molecules of halogens or interhalogens and form polyhalides.

$$I^{\odot} + I_2 \longrightarrow I_3^{\odot}$$

 $I_3^{\odot}$  (polyhalide) ion is stable in aqueous solution and in ionic crystals. More complex ions such as  $I_5^{\odot}$ ,  $I_7^{\odot}$  and  $I_9^{\odot}$  have been prepared. The  $Br_3^{\odot}$  and  $Cl_3^{\odot}$  ions are much less stable than  $I_3^{\ominus}$ .

Many polyhalides are known in which two or three different halogens are present such as  ${\rm ICl_2}^{\ominus}$ ,  ${\rm ICl_4}^{\ominus}$ ,  $({\rm IBrF})^{\ominus}$  and  $({\rm IBrCl})^{\ominus}$ .

31. Some of the monovalent ions made of electronegative atoms possessing properties similar to halide ions are known as pseudohalide ions. The corresponding dimers having no charge of these pseudohalide ions are called pseudohalogens.

Pseudohalide ions Pseudohalogens Cyanide ion  $(CN^{\Theta})$ (CN), Cyanogen Thiocyanate ion (SCN $^{\Theta}$ ) (SCN), Thiocyanogen Cyanate ion (OCN<sup>⊖</sup>) (OCN)<sub>2</sub> Oxycyanogen

32. Bleaching powder (CaOCl<sub>2</sub>·H<sub>2</sub>O) is also called calcium chlorohypochlorite because it is a mixed salt of hydrochloric acid and hypochlorous acid. It is represented as



It is obtained by the action of Cl<sub>2</sub> on slaked lime.

Bleaching powder loses its chlorine content by the action of dilute acids or carbon dioxide. The amount of chlorine obtained from the sample of a bleaching powder by this way is termed available chlorine. A good sample of bleaching powder contains 35-38% of available chlorine.

On long standing bleaching powder undergoes autooxidation into calcium chlorate and calcium chloride.

$$6CaOCl_2 \longrightarrow 5CaCl_2 + Ca(ClO_3)_2$$

The products do not have available chlorine.

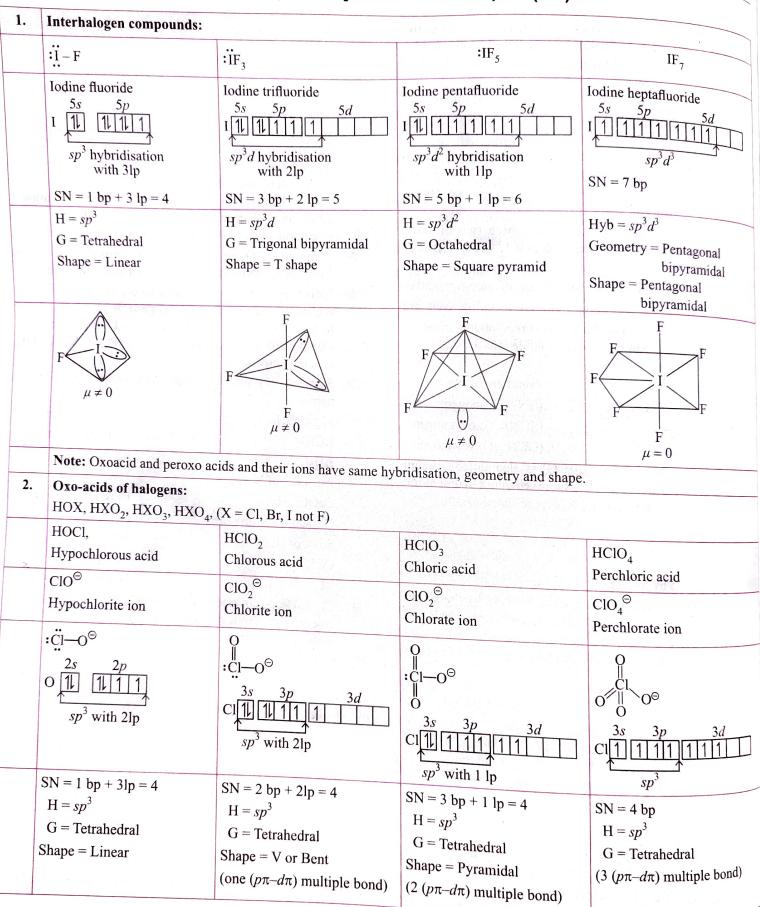
Thus, bleaching powder loses available chloring with time.

- 33. When a chloride is heated with conc.  $H_2SO_4$  in presence of solid K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> in a dry test tube, deep red vapours of chromyl chloride are evolved. When these vapours are passed through NaOH solution, the solution becomes yellow due to formation of sodium chromate. The solution is neutralised with acetic acid and on addition of lead acetate solution, a yellow precipitate of lead chromate is formed. This is a test of chloride ion and is known as chromyl chloride test.
- 34. Warming KClO<sub>3</sub> with conc. HCl gives a mixture of Cl<sub>2</sub> and ClO<sub>2</sub> known as euchlorine which is a bleaching agent.
- 35. Iodine shows an electropositive nature as it has the lowest ionisation potential among halogens. It has the tendency to lose electron or electrons to form  $I^{\oplus}$  and  $I^{3+}$  cations. Compounds such as ICl<sub>3</sub>, ICN, ICl<sub>3</sub>, IPO<sub>4</sub>, I(CH<sub>3</sub>COO)<sub>3</sub>, etc., are known.
- 36. Some of the products of halogens have been given special names.

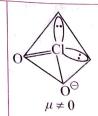
Anhydrone  $Mg(ClO_4)_2$ Berthelot's salt KClO<sub>3</sub> Ferming's salt KHF<sub>2</sub> Javelle water Aq. soln. of NaOCl Bleaching powder CaOCl,·H,O Euchlorine Cl<sub>2</sub> and ClO<sub>2</sub> mixture Spirit of salt Soln. of HCl Tear gas CCl<sub>3</sub>·NO<sub>2</sub> Oxymuriatic acid gas  $Cl_2$ 

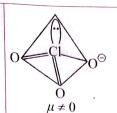
37. Cl<sub>2</sub> and F<sub>2</sub> do not react with starch solution. Br<sub>2</sub> gives yellow colour with starch solution and I2 gives deep blue colour with starch solution.

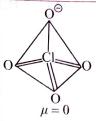
## Some Examples of Hybridisation of Group 17 (7e<sup>⊙</sup>)











Due to 4 equivalent resonance structures

#### Oxides of chlorine: 3.

Cl <sub>2</sub> O	
(0.S. = +1)	

Chlorine monoxide

$$ClO_2$$
(O.S. = +4)

Chlorine dioxide

$$Cl_2O_6$$
(O.S. = +6)

Chlorine hexoxide

(Red, explosive liquid)

 $Cl_2O_7$ 

(O.S. = +7)

Chlorine heptoxide

$$SN = 2 bp + 2 lp = 4$$

$$H = sp^3$$

$$G = T.H.$$

$$SN = 2 bp + 1 lp = 3$$

$$H = sp^3$$

G = Planar

Shape = V or bent or angular

$$SN = 4 bp$$

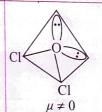
$$H = sp^3$$

Geometry = T.H.

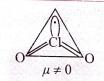
$$SN = 4 bp$$

$$H = sp^3$$

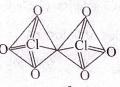
Geometry = T.H.



Angle 111°

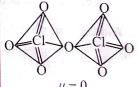


It contains unpaired electron, so it is coloured and paramagnetic and highly reactive. It contains three electron bonds, unlike NO2, it does not dimerise. [2  $(p\pi - d\pi)$  multiple bond]



$$\mu = 0$$

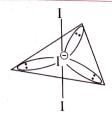
[6  $(p\pi - d\pi)$  multiple bond]



Shape = linear

[6  $(p\pi - d\pi)$  multiple bond]

## Polyhalide ion:



$$H = \frac{1}{2}(V + M) = \frac{1}{2}(7 + 2 + 1) = 5$$
 SN = 2 bp + 3lp = 5,  $H = sp^3d$ 

$$G = \text{T.b.p.}$$

## 4.1 INTRODUCTION

The five representative elements, fluorine (F), chlorine (Cl), bromine (Br), iodine (I) and astatine (At) constitute group 17, and are collectively known as halogens. The name 'halogen' is derived from Greek words, 'halo' which means 'salt' and 'genes' which means 'born', i.e. salt producers. The name halogen was given to them by Schweigger in 1811 as the salts (chlorides, bromides and iodides) of first three elements occur in sea water.

Halogens are non-metallic in nature. First member of this group, i.e. fluorine is the most active and most reactive halogen and hence is also known as **super halogen**.

## 4.2 OCCURRENCE AND ABUNDANCE

Halogens are highly reactive elements due to high electronegativity and hence do not occur in free or native state. All halogens except astatine mainly occur in earth's crust in the combined states as halides  $(X^{\Theta})$  although iodine occurs as iodate  $(IO_3^{\Theta})$ .

Fluorine is the thirteenth most abundant element by weight in the earth's crust, while chlorine is the twentieth. Fluorine and chlorine are reasonably abundant while bromine and iodine are comparatively rare.

Main source of **fluorine** is fluorspar or fluorite, CaF<sub>2</sub>. Other sources are fluoroapatite, 3Ca<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>, CaF<sub>2</sub> and cryolite, Na<sub>3</sub>[AlF<sub>6</sub>]. Small quantities are present in soil, river water plants and bones and teeth of animals.

The most abundant compound of **chlorine** is NaCl. Sea water contains chlorides, bromides and iodides of sodium, potassium, magnesium and calcium but is mainly NaCl solution (2.5% by

mass). The deposits of dried up seas contain sodium chloride, NaCl and carnallite, KCl.MgCl<sub>2</sub>·6H<sub>2</sub>O.

Bromine occurs in sea water and salt lakes as bromides of alkali or alkaline earth metals, e.g. KBr, MgBr<sub>2</sub> and NaBr.

Iodine never occurs free in nature. In combined state, it occurs as iodides and sodium iodate. Traces of compounds of this element are found in plants and animals in certain minerals and in sea water.

There are two main sources of iodine:

- a. Certain deep sea-weeds (Laminaria species). These plants contain 0.5% of iodine in their ashes (known as kelp of varee) in the form of iodates.
- b. Caliche or crude chile saltpetre (NaNO<sub>3</sub>) which contains about 0.2% of NaIO<sub>3</sub> (sodium iodate).

The less important sources of iodine are:

- a. Sodium, potassium and magnesium iodide in very small amounts are found in ores of lead and dolomite.
- **b.** Sea water contains iodides and organic compounds containing iodine.
- c. Thyroxine which is present in thyroid gland.
- d. Oil-well brines contain NaI.

# 4.3 ATOMIC AND PHYSICAL PROPERTIES

Some of the important atomic and physical properties of group 17 elements are given in Table 4.1 and are discussed in the following sections.

Table 4.1 Atomic and physical properties of halogens

Property	Fluorine	Chlorine	Bromine	lodine	Astatine <sup>#1</sup>
Symbol	F	Cl	Br	I	At
Atomic number	9	17	35	53	85
Atomic mass (g mol <sup>-1</sup> )	19.00	35.45	79.90	126.90	210
Electronic configuration	[He] $2s^2 2p^5$	[Ne] $3s^23p^5$	[Ar] $3d^{10}4s^24p^5$	[Kr] $4d^{10}5s^25p^5$	[Xe] $4f^{14}5d^{10}6s^{2}6$
Covalent radius (pm)	64	99	114	133	-
Ionic radius, $X^{\Theta}$ (pm)	133	184	196	220	_
Ionisation enthalpy (kJ mol <sup>-1</sup> )	1680	1256	1142	1008	-
Electron gain enthalpy (kJ mol <sup>-1</sup> )	-333	-349	-325	-296	-
Electronegativity#2	4.0	3.2	3.0	2.7	2.2
$\Delta_{\text{hyd}} \operatorname{H}^{\Theta}(X^{\Theta}) (\text{kJ mol}^{-1})$	515	381	347	305	_
	$F_2$	$Cl_2$	Br <sub>2</sub>	I <sub>2</sub>	-
Physical state	Gas	Gas	Liquid	Solid	_
Melting point (K)	54.4	172.0	265.8	386.6	_
Soiling point (K)	84.9	239.0	332.5	458.2	_
ensity (g cm <sup>3-</sup> )	1.5(85) <sup>#3</sup>	1.66#3	3.19(273)#3	4.94(293)#4	-
olour (gas)	Pale yellow	Yellow green	Brown red	Violet	
istance (X–X) (pm)	143	199	228	266	-

Bond dissociation enthalpy (kJ mol <sup>-1</sup> )	158.8	242.6	192.8	7.33 to . 151.1 11 topped	(4) 180 - <u>1</u> 0 (3)(6)
E <sup>O</sup> (V <sup>0</sup> )#5	+ 2.87	+ 1.36	+ 1.09	+ 0.54	
$\Delta_{\text{fus}} + (\text{kJ mol}^{-1})$	0.26	6.41	10.77	15.27	
$\Delta_{\text{vap}} \text{ (kJ mol}^{-1}\text{)}$	3.27	20.41	31.04	43.46	- 1.00.000

Note: #1: Radioactive; #2: Pauling scale; #3: For the liquid at temperatures (K) given in the parentheses. #4: Solid; #5: The half cell reaction is  $X_{2(g)} + 2e^{\Theta} \longrightarrow 2X_{(aq)}^{\Theta}$ 

## 4.3.1 ELECTRONIC CONFIGURATION

The general electronic configuration of group 17 elements is  $ns^2np^5$ , i.e. all the group 17 elements have seven electrons in their valence shell, i.e., one electron short of the next noble gas.

## 4.3.2 ATOMIC AND IONIC RADII

Halogens have the smallest atomic radii in their respective periods. This is due to the fact that atomic radii decrease, on moving from the left to the right in the periodic table, with increase in effective nuclear charge.

Down the group (↓) i.e. from F to At, atomic radii increase due to increase in number of shells, the effective nuclear charge decreases.

Atomic radii: F < Cl < Br < I

The ionic radii of the halide ion  $(X^{\Theta})$  is always greater than the corresponding halogen (X) atom.

This is because of the fact that with the addition of an electron, effective nuclear charge decreases and the electron cloud expand.

Down the group  $(\downarrow)$ , ionic radii also increase.

Ionic radii:  $F^{\Theta} < Cl^{\Theta} < Br^{\Theta} < I^{\Theta}$ 

## 4.3.3 IONISATION ENTHALPY

The ionisation enthalpies of halogens are very high. Thus they have very little tendency to lose electron to form  $X^{\oplus}$  cation.

Down the group (\$\sqrt{\psi}\$), i.e. from F to I, ionisation enthalpy decreases due to increase in the size of halogen iodine, having the lowest value of ionisation enthalpy, shows some tendency to form  $I^{\oplus}$ , e.g. in  $[I(pyridine)_2]^{\oplus}(NO_3)^{\bigcirc}$ .  $I^{\oplus}$  is stabilised by forming a complex with Lewis base, pyridine.

lonisation enthalpy: F > Cl > Br > I

## 4.3.4 ELECTRON GAIN ENTHALPY

Halogens have maximum negative electron gain enthalpy in their respective periods. This is due to the fact that halogens are just one electron short to acquire the stable electronic configuration of next <sup>noble</sup> gas. Therefore, they have strong tendency to gain an electron.

Down the group (\$\sqrt{}\$), electron gain enthalpies become less and less negative with the increase in the size of the halogen. However, electron gain enthalpy of F is less negative than Cl. This is due to small size of F atom. As a result, there are strong interelectronic repulsions in the relatively small 2p orbitals of F and thus incoming electrons experience much less attraction.

Electron gain enthalpy: Cl > F > Br > I.

#### 4.3.5 ELECTRONEGATIVITY

Halogens have very high value of electronegativities in their respective periods due to small size and high nuclear charge. Fluorine has been assigned the highest electronegativity of 4.0.

Down the group  $(\downarrow)$ , i.e. from F to I, electronegativity decreases due to increase in size of halogen atom. Consequently, the nonmetallic character decreases from F to I.

Metallic character is observed in iodine as it forms in few cases a positive ion and has a metallic lustre.

Electronegativity: F > Cl > Br > I

Non-metallic character: F > Cl > Br > I

#### 4.3.6 ATOMICITY

All halogens exist as diatomic  $(X_2)$  molecules, with X-X bond. This is due to the fact that each halogen has one electron less than the next nearest noble gas. Hence they are highly reactive and readily share their unpaired electron with other atom to form a covalent bond.

#### 4.3.7 PHYSICAL STATE

At room temperature, fluorine and chlorine are gases, bromine is liquid and iodine is a solid. At atmospheric pressure, I2 solid sublimes without melting. The main reason for the change in physical state from gas (F2 and Cl2) to liquid (Br2) to solid (I2) is that down the group (\$\dpsi\$) with increase in atomic size, ease of polarisation of outer shell electrons by adjacent nuclei increases. This results in greater intermolecular attractive forces. Hence F, and Cl<sub>2</sub> exist as gases, Br<sub>2</sub> is a liquid and I<sub>2</sub> is a solid. On account of weak intermolecular forces, i.e. van der Waals forces of attraction, the halogens are volatile in native.

## 4.3.8 MELTING POINTS AND BOILING POINTS

Due to weak van der Waals forces of attraction between the dimeric halogen molecules, the melting points and boiling points are very low. Down the group (\$\dpsi\$), with the increase in size, ease of polarisation increases and hence melting point and boiling point increase.

Melting point:  $F_2 < Cl_2 < Br_2 < I_2$ Boiling point:  $F_2 < Cl_2 < Br_2 < I_2$ 

## 4.3.9 ENTHALPY OF FUSION AND VAPOURISATION

Enthalpy of fusion and vapourisation of halogens have low values due to weak van der Waals forces of attraction between halogen molecules  $(X_2)$ 

Down the group ( $\downarrow$ ), from  $F_2$  to  $I_2$ , with the increase in size, the ease of polarisation increases and hence  $\Delta_{fus}H^{\Theta}$  and  $\Delta_{vap}H^{\Theta}$ 

$$\begin{array}{ll} \Delta_{\rm fus} {\rm H}^{\Theta} : & {\rm F_2} < {\rm Cl_2} < {\rm Br_2} < {\rm I_2} \\ \Delta_{\rm vap} {\rm H}^{\Theta} : & {\rm F_2} < {\rm Cl_2} < {\rm Br_2} < {\rm I_2} \end{array}$$

#### 4.3.10 NON-METALLIC CHARACTER

Halogens are non-metallic in nature, due to their very high values of ionisation enthalpy and electronegativity. Down the group, non-metallic character decreases due to decrease in the value of ionisation enthalpy and electronegativity. In fact, iodine is a solid and possesses metallic lustre.

## 4.3.11 BOND DISSOCIATION ENTHALPY

Halogens exist as diatomic molecules. It would be expected that bond dissociation enthalpy, i.e. the energy required to dissociate the halogen molecule (X2) into halogen atom (X) would decrease down the group  $(\downarrow)$ . This is due to the fact that with the increase in atomic size, the effective overlap of orbitals resulting in X-X bond formation decreases. Cl<sub>2</sub>, Br<sub>2</sub> and I<sub>2</sub> show the expected trend, but the bond dissociation enthalpy of F<sub>2</sub> is less than Br<sub>2</sub> and Cl<sub>2</sub>.

$$Cl_2 > Br_2 > F_2 > I_2$$

Abnormally low bond dissociation enthalpy of F2 is largely responsible for its high reactivity. Two different explanations have been suggested for low bond dissociation enthalpy of F<sub>2</sub>:

The large electron-electron repulsions between the lone pairs of electrons on the two fluorine atoms weaken the bond.

### 4.3.12 COLOUR

All the halogen molecules are coloured and the colour changes with increasing size of the halogen molecule.

Halogen	F <sub>2</sub>	Cl <sub>2</sub>	Br <sub>2</sub>	I <sub>2</sub>
Colour	Pale yellow	Yellow green	Reddish brown	Violet

The colour is due to absorption of light in the visible region. The energy acquired in this manner excites the valence electron from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO), i.e. transition from  $\pi^*$  to  $\sigma^*$  molecular orbital.

On de-excitation, the energy of transmitted light falls in visible region and the colour of halogen is actually the colour of this transmitted light, i.e. halogens have complementary colour.

The excitation energy, i.e. the amount of energy required for the excitation decreases progressively from F<sub>2</sub> to I<sub>2</sub>, with the increase in atomic size. conversely, energy of transmitted light increases progressively. Hence there is progressive deepening of colours down the group, i.e. from  $F_2$  to  $I_2$ .

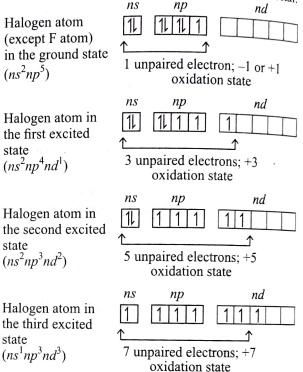
The F<sub>2</sub> molecule is small, in which the valence electrons are held tightly. Thus it absorbs high energy violet radiation and appears pale yellow.

The larger I2 molecule absorbs low-energy yellow and green radiations and appears violet. Change in colour on moving down the group is known as bathochromic shift.

## 4.4 CHEMICAL PROPERTIES

## 4.4.1 NATURE OF BONDS AND OXIDATION STATES

When the halogen atom combines with an element of lesser electronegativity, it shows -1 oxidation state, on the other hand when it combines with an element of higher electronegativity, when it combines with an element of higher electronegativity, when it combines with an element of higher electronegativity, when it combines with an element of higher electronegativity when it combines with an element of higher electronegativity. it exhibits +1 oxidation state. Fluorine, having the highest electronegativity, shows -1 oxidation state, except in HOF, where the oxidation state of F is +1. The other halogens i.e. Cl, Br and I, in addition to an oxidation state of -1, also shows positive oxidation +1 and highest oxidation states of +3, +5 and +7 as the electrons in *ns* and *np* orbitals can be promoted to vacant *nd* orbital.



F atom has no d-orbitals in the valency shell, thus, it cannot have any excited state and cannot show any of the higher oxidation states.

In addition to the above-mentioned positive oxidation states. Cl, Br and I also show an oxidation state of +4 (in ClO<sub>2</sub>) and +6 (in Cl<sub>2</sub>O<sub>6</sub> and ClO<sub>3</sub>) while Br shows an oxidation state of +4 (11  $BrO_{2}$ ).

## 4.4.2 OXIDISING POWER

Electron affinity is the tendency of the atoms to gain electrons Chlorine has the highest electron affinity. Oxidation may be regarded as the removal of electrons, so that an oxidising agent gains electrons. Thus the halogens, which have strong tendency to accept an electron, act as strong oxidising agents, and their oxidising power decreases from fluorine to iodine.

$$E^{\Theta}(V)$$
 +2.87 +1.36 +1.09 +0.54

The strength of oxidising agent (that is oxidation potential depends on several energy terms. The oxidation potential is the energy change between the element in its standard state and in its hydrated ions. For iodine, the change is from

$$\frac{1}{2} I_{2(s)}$$
 to  $I_{\text{(hydrated)}}^{\Theta^*}$ 

$$\frac{\frac{1}{2}I_{2(s)} \xrightarrow{\frac{1}{2}\Delta_{fus}H^{\Theta}} \frac{1}{2}I_{2(l)} \xrightarrow{\frac{1}{2}\Delta_{vap}H^{\Theta}} \frac{1}{2}I_{2(g)}}{I_{(hyd)} \xleftarrow{\Delta_{hyd}H^{\Theta}} I_{(g)} \xleftarrow{\Delta_{c.g.}H^{\Theta}} I_{(g)}$$

$$\mathcal{E} = \frac{1}{2} \Delta_{fus} H^{\Theta} + \frac{1}{2} \Delta_{vap} H^{\Theta} + \frac{1}{2} \Delta_{diss} H^{\Theta} + \Delta_{eg} H^{\Theta} + \Delta_{hyd} H^{\Theta}$$

 $_{\text{Fot bromine}},$  the change is from  $\frac{1}{2}\text{Br}_{2(\text{l})}$  to  $\text{Br}_{\text{(hyd)}}^{\Theta}.$ 

$$\begin{array}{c} \frac{1}{2}\mathrm{Br}_{2(l)} \xrightarrow{\begin{array}{c} \frac{1}{2}\Delta_{\mathrm{vap}}H^{\bigodot} \\ \end{array}} \underbrace{\frac{1}{2}\mathrm{Br}_{2(g)} \xrightarrow{\begin{array}{c} \frac{1}{2}\Delta_{\mathrm{diss}}H^{\bigodot} \\ \end{array}}}_{Br_{(g)}} \mathrm{Br}_{(g)} \\ \\ \mathrm{Br}_{(hyd)} \xleftarrow{\Delta_{hyd}H^{\bigodot}}_{g)} \mathrm{Br}_{(g)} \end{array}$$

$$E = \frac{1}{2} \Delta_{vap} H^{\Theta} + \frac{1}{2} \Delta_{diss} H^{\Theta} + \frac{1}{2} \Delta_{eg} H^{\Theta} + \Delta_{hyd} H^{\Theta}$$

For fluorine and chlorine, the change is from

$$\frac{1}{2}F_{2(g)} \text{ to } \frac{1}{2}F_{2(hyd)} \text{ and } \frac{1}{2}Cl_{2(g)} \text{ to } Cl^{\Theta}_{(hyd)}$$

$$E = \frac{1}{2}\Delta_{diss}H^{\Theta} + \Delta_{eg}H^{\Theta} + \Delta_{hyd}H^{\Theta}$$

Chlorine has highest electron gain enthalpy, so gaseous Cl can accept electron most readily. However, chlorine is not the strongest oxidising agent. Fluorine acts as the strongest oxidising agent and the oxidising power decreases from  $F_2$  to  $I_2$ .

Oxidising power:

$$F_2 > Cl_2 > Br_2 > I_2$$

This is due to:

- 1. F<sub>2</sub> has a low enthalpy of dissociation due to weakness of F-F bond.
- 2.  $F_2$  has a high free energy of hydration due to smallest size of  $F^{\Theta}$  ion.

Fluorine will oxidise other halide ions to halogens in solution or when dry.

$$F_2 + 2X^{\Theta} \longrightarrow 2F^{\Theta} + X_2 (X = Cl, Br, I)$$

Similarly, chlorine gas will displace  $Br^{\Theta}$  and  $I^{\Theta}$  from solution.

$$Cl_{2(g)} + X^{\Theta}_{(hyd)} \longrightarrow Cl^{\Theta}_{(hyd)} + X_2 (X = Br \text{ or } I)$$

This is the basis of commercial extraction of bromine from sea water.

In general, any halogen of lower atomic number will oxidise the halide ion of higher atomic number.

Thus, a stronger oxidising halogen can be used to prepare a weaker oxidising halogen from its anion. For example,  $Cl_2$  water is used to produce  $Br_2$  and  $I_2$  from  $Br^{\ominus}$  and  $I^{\ominus}$  solutions respectively.

The relative oxidising power of halogens can further be illustrated by their reactions with water.  $F_2$  oxidises  $H_2O$  to  $O_2$  and  $O_3$  whereas  $Cl_2$  and  $Br_2$  react with water to form corresponding hydrohalic and hypohalous acids.

$${}^{2F_{2(g)}} + 2H_{2}O_{(l)} \xrightarrow{\mathcal{A}} 4H^{\oplus}_{(aq)} + 4F^{\ominus}_{(aq)} + O_{2(g)}$$

$${}^{3F_{2(g)}} + 3H_{2}O_{(l)} \xrightarrow{\mathcal{A}} 6H^{\oplus}_{(aq)} + 6F^{\ominus}_{(aq)} + O_{3(g)}$$

$$\begin{aligned} \text{Cl}_{2(g)} + \text{H}_2\text{O}_{(l)} & \longrightarrow \text{HCl}_{(aq)} + \text{HOCl}_{(aq)} \\ & \text{Hypochlorous acid} \end{aligned}$$

$$Br_{2(g)} + H_2O_{(1)} \longrightarrow HBr_{(aq)} + HOBr_{(aq)}$$
Hypobromous acid

The reaction of  $I_2$  and  $H_2O$  is non-spontaneous. In fact,  $I^{\odot}$  ions can be oxidised by  $O_2$  in acidic medium which is just the reverse of reaction observed with  $F_2$ .

$$4H_{(aq)}^{\Theta} + O_{2(g)} + 4H_{(aq)}^{\oplus} \longrightarrow 2I_{2(s)} + 2H_{2}O_{(1)}$$

The halide ions act as reducing agents.  $I^{\odot}$  ion does not show any reducing nature but  $CI^{\odot}$ ,  $Br^{\odot}$  and  $I^{\odot}$  ions act as reducing agents and their reducing nature is in increasing order.

Reducing nature: 
$$F^{\bigcirc} < Cl^{\bigcirc} < Br^{\bigcirc} < I^{\bigcirc}$$

## ILLUSTRATION 4.1

Explain

- **a.** Addition of Cl<sub>2</sub> to KI solution gives it a violet colour but excess of Cl<sub>2</sub> turns it colourless.
- **b.** Slow Cl<sub>2</sub> can be prepared from HCl and HCl from Cl<sub>2</sub>?
- c. F<sub>2</sub> is a non-metal whereas I<sub>2</sub> shows some metallic properties.
- d. Metal fluorides are more ionic than metal chlorides.

Sol.

**a.** Since  $I^{\Theta}$  is a stronger oxidising agent thus  $Cl_2$  releases  $I_2$  and gives violet colour.

$$\text{Cl}_2 + 2\text{I}^{\Theta} \rightarrow 2\text{Cl}^{\Theta} + \text{I}_2 \text{ (violet)}$$

But excess of  $\operatorname{Cl}_2$  oxidises  $\operatorname{I}_2$  to colourless Iodic acid

$$5\text{Cl}_2 + \text{I}_2 + 6\text{H}_2\text{O} \rightarrow 2\text{HIO}_3 + 10\text{HCl}$$

(colourless)

- **b.** (i)  $MnO_2 + 4HCl \rightarrow MnCl_2 + Cl_2 + 2H_2O$ 
  - (ii)  $Cl_2 + H_2 \xrightarrow{Sunlight} 2HCl$
- **c.** Due to high I.E. and small size of F, it has no tendency to lose  $e^-$ . Whereas, due of low I.E. and large size of I, it can lose  $e^-$ 's and shows electropositive nature i.e., metallic nature.
- d. According to Fajan's rule:
  - (i) Small cation, large anion more covallent character.
  - (ii) Large cation, small anion ∞ more ionic character. Size of Cl<sup>©</sup> > Size of F<sup>©</sup>

Thus metal fluorides are more ionic than metal chlorides.

## 4.5 CHEMICAL CHARACTERISTICS

Halogens are highly reactive non-metallic due to:

- a. Low bond dissociation enthalpy  $(X_2 \longrightarrow 2X)$ : Halogens have low bond dissociation enthalpy as compared to common molecules like  $H_2$ ,  $O_2$ ,  $N_2$ , etc. Therefore, they readily dissociate into atoms and react with other substances readily.
- b. High negative electron gain enthalpies: Due to high negative electron gain enthalpies, halogens have a very strong tendency to gain an electron and thus are very reactive,

They react with metals and non-metals to form halides. However, down the group  $(\downarrow)$ , the reactivity decreases in the order:  $F_2 > Cl_2 > Br_2 > I_2$ .

### 4.5.1 REACTIVITY TOWARDS HYDROGEN

All the halogens react with hydrogen to form volatile, covalent hydrides of formula HX. These hydrides are called hydracids or halogen acids. The activity of halogens towards hydrogen decreases from fluorine to iodine.

Hydrogen combines explosively with fluorine even in dark. It combines with chlorine in presence of sunlight and with bromine on heating. Hydrogen combines with iodine on heating and in presence of a catalyst. The reaction with iodine is reversible and incomplete.

#### 4.5.2 REACTIVITY TOWARDS OXYGEN

Halogens form many binary compounds with oxygen but most of them are unstable.

Compounds of fluorine and oxygen are referred to as fluorides of oxygen and not oxides of fluorine as fluorine is more electronegative than oxygen. The compounds of Cl, Br and I with oxygen are termed as oxides.

Chlorine, bromine and iodine form oxides in which the oxidation states of halogens range from +1 to +7. Chlorine forms the largest number of oxides while iodine forms the least. In these binary compounds, the bonds are mainly covalent due to small difference in electronegativity between the halogens and oxygen; the bond polarity, however, increases from Cl to I. The stability of oxides of iodine is greater than those of chlorine while bromine oxides are the least stable. Iodine—oxygen bond is stable due to greater polarity of the bond while the stability of the chlorine—oxygen bond is due to multiple bond formation involving *d*-orbitals of the chlorine atom. Bromine being in between lacks both these characteristics. Thus, the stability of oxides of halogens decreases in the order: I > Cl > Br. Further the higher oxides of halogens tend to be more stable than the lower ones.

#### 4.5.3 REACTIVITY TOWARDS HALOGENS

Halogens react with each other to form a number of compounds known as interhalogen compounds.

#### 4.5.4 REACTIVITY TOWARDS WATER

Fluorine decomposes water very readily even at low temperature and in dark forming mixture of O<sub>2</sub> and O<sub>3</sub>, Cl<sub>2</sub> decomposes water in presence of sunlight while bromine decomposes water very slowly in presence of sunlight. Iodine does not decompose water.

$$X_2 + H_2O \xrightarrow{Sunlight} + HX + HOX$$
  
(Cl<sub>2</sub> or Br<sub>2</sub>)

$$3F_2 + 3H_2O \longrightarrow 6HF + O_3$$

$$2F_2 + 2H_2O \longrightarrow 4HF + O_2$$
  
 $I_2 + H_2O \longrightarrow No reaction$ 

## 4.5.5 REACTIVITY TOWARDS METALS AND NON-METALS

Due to high oxidising power, halogens combine directly with most metals to form their corresponding halides. Nearly all metals combine with  $F_2$  either in cold or on heating to form fluorides. Chlorine combines with large number of metals but slowly. Bromine and iodine do not react with non-metals, like Au,  $P_{tand}$  even with less active metals.

As expected, the ionic character of the M-X bond, decreases in the order:

$$M-F > M-Cl > M-Br > M-I$$

This is due to a corresponding decrease in the electro-negativity of the halogen from F to I. However, if the metal exhibits more than one oxidation states, the halide in the higher oxidation state will be more covalent than the one in the lower oxidation state. For example, SnCl<sub>4</sub>, PbCl<sub>4</sub>, SbCl<sub>5</sub>, UF<sub>6</sub> are more covalent than SnCl<sub>2</sub>, PbCl<sub>2</sub>, SbCl<sub>3</sub> and UF<sub>4</sub> respectively.

Halogens also combine with a number of non-metals like § P, As, etc. The reactivity decreases from fluorine to chlorine For example, sulphur forms hexafluoride with fluorine (SF<sub>6</sub>), tetrachloride with chlorine (SCl<sub>4</sub>) and dibromide with bromine (SBr<sub>2</sub>) and there is no reaction between sulphur and iodine.

# 4.6 ANOMALOUS BEHAVIOUR OF FLUORINE

Fluorine, the first member of group 17 elements, differs from other members of its group, due to the following reasons:

- Smallest size of the atom
- Highest electronegativity
- Absence of *d*-orbitals in its valence shell
- Low bond-dissociation enthalpy of F<sub>2</sub> molecule.

The main points of difference are as follows:

- Reactivity: Fluorine is the most reactive as bond dissociation energy of F—F bond is low. X—X bond is the stronger in Cl<sub>2</sub> and Br<sub>2</sub>.
- 2. Maximum covalency of fluorine is one as there is no *d*-orbid in its valence shell. Other members can have maximum covalency of 7 because of vacant *d*-orbitals.
- 3. HF is a weak acid in comparison to HCl, HBr and HI under similar circumstances. HF is a liquid (b.pt. 19°C) while HCl. HBr and HI are gases under ordinary conditions. This is due to presence of hydrogen bonding in HF while hydrogen bonding is not present in HCl, HBr and HI.
- **4. Oxidation state:** Since it is the most electronegative element it shows an oxidation state of -1, except +1 in HOF. Further, it does not show any higher oxidation states (positive or negative) because of the absence of d-orbitals in its valence shell. Other members, however, show both negative oxidation state of -1 and different positive oxidation states of +1, +3, +5 and +7.

Since fluorine usually does not show positive oxidation states, therefore,  $F_2$  does not undergo disproportionation reactions in the alkaline medium while other halogens do.  $X_2 + 2NaOH \xrightarrow{Cold} NaX + NaOX + H_2O \text{ (where X = Cl,Br or I)}$   $3X_2 + 6NaOH \xrightarrow{Hot} 5 NaX + NaXO_3 + 3H_2O$ 

- (where X = Cl, Br or I)
- 5. Hydrogen bonding: Hydrogen bonding is a distinct phenomenon observed in some fluorine compounds due to small atomic size and high electronegativity of fluorine.
  - HF is a liquid with a boiling point of 293 K while other halogen halides are gases under ordinary conditions with low boiling points.
  - ii. HF is a weak acid as compared to other halogen acids which are strong and highly ionised. This is due to higher dissociation energy of H-F bond and molecular association due to hydrogen bonding in HF.
  - iii. Due to hydrogen bonding, HF can form acid salts of the type KHF<sub>2</sub>, i.e.,  $[K^{\oplus} (F-H-F)^{\ominus}]$  while other halogen acids do not form such compounds.
- 6. Nature of compounds: Due to its highest electronegativity, fluorine has the highest tendency to form ionic compounds and thus fluorides have the maximum ionic character. For example, AIF<sub>3</sub> is ionic whereas other halides of aluminium are covalent.
- 7. Oxidising power: Fluorine has the highest electrode potential. Thus, it is reduced most easily and hence acts as the strongest oxidising agent among the halogens. It brings about highest oxidation state of other elements with which it combines. For example, with sulphur it gives SF<sub>6</sub> and with osmium it gives OsF<sub>8</sub>. Other halogens do not always bring about the highest oxidation state of the element. It can oxidise most of the other elements, including some of the noble gases (Kr and Xe).
- 8. Reactivity of halogen acids: HF although weak, is the most reactive of all halogen acids. It can attack glass because of its ability to displace oxygen from silicates to form fluorosilicates.

 $Na_2SiO_3 + 6HF \longrightarrow H_2SiF_6 + 2NaF + 3H_2O$ 

That is why HF is used for etching of glass, in marking thermometers, burettes, etc. Other halogen acids, i.e., HCl, HBr and HI do not give this reaction.

Due to the above special properties of fluorine, it is usually called as super halogen.

- AgF is soluble in water while AgCl, AgBr and AgI are insoluble in water. Similarly, calcium fluoride is insoluble and other halides of calcium are soluble.
- 10. Fluorine combines with sulphur to form  ${\rm SF}_6$  but no other halogen forms the hexahalide with sulphur.
- 11. Fluorine does not form any oxyacid but other halogens form a number of oxyacids.
- 12. It directly combines with carbon while other halogens do not react even under drastic conditions.

- 13. Ozone is formed when fluorine decomposes water. Ozone is not formed when other halogens react with water.
- 14. Fluorine does not form any oxysalt when it reacts with alkalies while other halogens form oxysalts with alkalies.
- 15. Fluorides are more stable than corresponding chlorine compounds. For example, UF<sub>6</sub> is more stable than UCl<sub>6</sub>, NF<sub>3</sub> is non-explosive while NCl<sub>3</sub> is highly explosive.
- **16.** The fluoride ion has a great tendency to form complex ions, e.g.,  $[AIF_6]^{3-}$ ,  $[FeF_6]^{3-}$ . The remaining halide ions show this tendency to a much lesser extent.
- 17. Fluorine does not have a vacant *d*-orbital in valence shell, therefore it does not combine with F ion to form polyfluoride ions like  $\operatorname{Cl}_3^{\ominus}$ ,  $\operatorname{Br}_3^{\ominus}$ ,  $\operatorname{I}_3^{\ominus}$ ,  $\operatorname{I}_5^{\ominus}$ , etc.

## ILLUSTRATION 4.2

- **a.** Halogens have maximum negative gain enthalpy in the respective periods of the periodic table. Why?
- b. Although electron gain enthalpy of fluorine is less negative as compared to chlorine, fluorine is a stronger oxidising agent than chlorine. Why?
- c. Fluorine exhibits only -1 oxidation state, whereas other halogens exhibit +1, +3, +5 and +7 oxidation states also. Explain.

#### Sol.

- a. Halogens have the smallest size in their respective periods and therefore high effective nuclear charge. As a consequence, they readily accept one electron to acquire noble gas configuration.
- b. Fluorine is a stronger oxidising agent than chlorine, due to:
  - i. Low enthalpy of dissociation of F-F bond
  - ii. High hydration enthalpy of fluorine.
- c. Fluorine is the most electronegative element and cannot exhibit positive oxidation state. Other halogens have vacant *d*-orbitals and therefore, can expand their octets and show +1, +3, +5 and +7 oxidation states also.

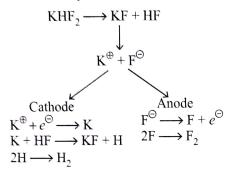
## 4.7 FLUORINE

Fluorine presented many difficulties in its isolation and was isolated by Moissan in 1886. The reasons for its late discovery were its high reactivity and non-conducting nature of hydrofluoric acid. Fluorine attacked the material of the vessels used for its isolation. Carbon vessel was attacked with formation of CF<sub>4</sub> and platinum vessel was reduced to chocolate powder. The vessels of other metals were also affected. The platinum and carbon could not be used as electrodes. Another difficulty experienced was that when the electrolysis of aqueous HF acid was carried out, hydrogen and ozone were obtained and when anhydrous hydrofluoric acid was tried it was found to be a bad conductor of electricity.

Moissan finally isolated fluorine by the electrolysis of anhydrous hydrofluoric acid in the presence of potassium hydrogen fluoride using Pt–Ir alloy vessel at –23°C. The electrodes used were also of Pt–Ir alloy.

Modern methods of isolation: In modern methods, fluorine is prepared by electrolysis of a fused fluoride (usually potassium hydrogen fluoride, KHF<sub>2</sub>). The electrolytic cells are made of copper, nickel or monel metal. The anode is generally of graphite and the fluorine set free contains some carbon tetrafluoride.

#### Reactions in the electrolytic cell



Following precautions should be taken in the preparation of fluorine:

- i. The electrolyte must be completely dry. In presence of moisture, the evolved fluorine reacts with moisture to form O<sub>2</sub> and O<sub>3</sub>.
- ii. The parts of the apparatus which come in contact with fluorine must be free from oil and greese.
- **iii.** The vessel in which fluorine is collected should also be absolutely dry.
- iv. The gas must be made free from HF before storing by passing through sodium fluoride (NaF) otherwise HF will attack vessel. HF is more corrosive and reactive than fluorine.

#### **Properties:**

#### (A) Physical properties

- 1. The gas is pale greenish yellow in colour. It can be condensed to yellow liquid at -188°C and pale yellow solid at -223°C.
- 2. It has pungent odour resembling that of a mixture of ozone and chlorine. It is a poisonous gas but less poisonous than HF gas. It is the most reactive element.

#### (B) Chemical properties

1. Fluorine reacts vigorously with water to give  $O_2$  and  $O_3$ .

$$2H_2O + 2F_2 \longrightarrow 4HF + O_2$$
  
 $3H_2O + 3F_2 \longrightarrow 6HF + O_3$ 

 Fluorine reacts with dilute alkalies to form oxygen difluoride (OF<sub>2</sub>) and with conc. alkalies O<sub>2</sub> is formed.

$$2F_2 + 2NaOH \longrightarrow OF_2 + 2NaF + H_2O$$
  
 $2F_2 + 4NaOH \longrightarrow 4NaF + 2H_2O + O_2$ 

3. It acts as a strong oxidising agent. It oxidises chlorates to perchlorates, iodates to periodates and bisulphates to peroxysulphates.

$$KClO_3 + F_2 + H_2O \longrightarrow KClO_4 + H_2F_2$$
  
 $KIO_3 + F_2 + H_2O \longrightarrow KIO_4 + H_2F_2$   
 $2NaHSO_4 + F_2 \longrightarrow Na_2S_2O_8 + 2HF$ 

4. It attacks glass at about 100°C forming SiF<sub>4</sub>. H<sub>OWeVeV</sub> the attack of dry fluorine is slow. At low temperatures, d<sub>η</sub> fluorine can be stored in dry glass vessel.

#### Uses:

- 1. It is used as an insecticide.
- It is extensively used for the preparation of various fluoring compounds which have wide applications.
  - a. Freon, CCl<sub>2</sub>F<sub>2</sub> (dichloro difluoro methane), is used in refrigerators and cold storage plants.
  - b. Teflon  $(C_2F_4)$ , a new plastic, has a very high  $electric_{al}$  resistance and is used as insulating material in cables Teflon is not affected by acids, alkalies and strong oxidising agents.
  - c. H<sub>2</sub>F<sub>2</sub> is used for etching of glass and for removing silication iron castings.

$$SiO_2 + 2H_2F_2 \longrightarrow SiF + 2H_2O$$

- d. UF<sub>6</sub> is used in the separation of <sup>235</sup>U from natural uranium by diffusion method.
- e. SF<sub>6</sub> has insulating properties. It is used in X-ray and high voltage machines.
- f. Sodium fluoroacetate is used as a rat poison.
- g. NaF and Na<sub>3</sub>AlF<sub>6</sub> (cryolite) are used as insecticides.
- h. CuF<sub>2</sub> is used in the ceramic industry and as a flux in soldering, welding and glazing.

## 4.8 CHLORINE

Chlorine was discovered by **Scheele** in 1774 by the action of HCl on MnO<sub>2</sub>. **Berthollet** named this gas oxymuriatic acid gas since he thought it to be an oxide of muratic acid (old name of HCl). In 1810, **Davy** established its elementary nature and named it chloring on account of its greenish yellow colour (**Greek word**, 'chloris' which means 'greenish yellow').

### Preparation:

- 1. By the oxidation of hydrochloric acid: The oxidising agents which can be used are MnO<sub>2</sub>, PbO<sub>2</sub>, Pb<sub>3</sub>O<sub>4</sub> (red lead), KMnO<sub>4</sub> (potassium permanganate), K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> (potassium dichromate), NaOCl (sodium hypochlorite), O<sub>3</sub>, etc. In all these reactions, HCl acts as a reducing agent.
  - i. With MnO<sub>2</sub>:

$$MnO_2 + 2HCl \longrightarrow MnCl_2 + H_2O + [O]$$

$$2HCl + [O] \longrightarrow H_2O + Cl_2 \uparrow$$

$$MnO_2 + 4HCl \longrightarrow MnCl_2 + 2H_2O + Cl_2$$

ii. With PbO<sub>2</sub>:

$$PbO_2 + 4HCl \longrightarrow PbCl_2 + 2H_2O + Cl$$

iii. With red lead, Pb3O4:

$$Pb_{3}O_{4} + 6HCl \longrightarrow 3PbCl_{2} + 3H_{2}O + [O]$$

$$2HCl + [O] \longrightarrow H_{2}O + Cl_{2} \uparrow$$

$$Pb_{3}O_{4} + 8HCl \longrightarrow 3PbCl_{2} + 4H_{2}O + Cl_{2} \uparrow$$

iv. With KMnO<sub>4</sub>:  

$$2KMnO_4 + 6HCl \longrightarrow 2KCl + 2MnCl_2 + 3H_2O + [O]$$

$$10HCl + 5[O] \longrightarrow 5H_2O + 5Cl_2\uparrow$$

$$2KMnO_4 + 16HCl \longrightarrow 2KCl + 2MnCl_2 + 8H_2O + 5Cl_2\uparrow$$
v. With K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>:  

$$K_2Cr_2O_7 + 8HCl \longrightarrow 2KCl + 2CrCl_3 + 4H_2O + 3[O]$$

$$6HCl + 3[O] \longrightarrow 3H_2O + 3Cl_2\uparrow$$

$$K_2Cr_2O_7 + 14HCl \longrightarrow 2KCl + 2CrCl_3 + 7H_2O + 3Cl_2\uparrow$$
vi. With NaOCl:

NaOCl 
$$\longrightarrow$$
 NaCl + [O]  
2HCl + [O]  $\longrightarrow$  H<sub>2</sub>O + Cl<sub>2</sub>  
NaOCl + 2HCl  $\longrightarrow$  NaCl + H<sub>2</sub>O + Cl<sub>2</sub> $\uparrow$   
vii. O<sub>3</sub> + 2HCl  $\longrightarrow$  O<sub>2</sub> + H<sub>2</sub>O + Cl<sub>2</sub> $\uparrow$ 

2. By the action of mineral acids or CO<sub>2</sub> on bleaching powder.  $CaOCl_2 + H_2SO_4 \longrightarrow CaSO_4 + H_2O + Cl_1 \uparrow$ 

$$CaOCl_2 + 2HCl \longrightarrow CaCl_2 + H_2O + Cl_2 \uparrow$$
  
 $CaOCl_2 + CO_2 \longrightarrow CaCO_3 + Cl_2$ 

3. In laboratory, Cl<sub>2</sub> is prepared by heating with concentrated  $H_2SO_4$  in presence of MnO<sub>2</sub>.

$$\begin{aligned} &\operatorname{MnO_2} + \operatorname{H_2SO_4} \longrightarrow \operatorname{MnSO_4} + \operatorname{H_2O} + [\operatorname{O}] \\ &[\operatorname{NaCl} + \operatorname{H_2SO_4} \longrightarrow \operatorname{NaHSO_4} + \operatorname{HCl}] \times 2 \\ &2\operatorname{HCl[O]} \longrightarrow \operatorname{H_2O} + \operatorname{Cl} \uparrow \end{aligned}$$

$$2\text{NaCl} + \text{MnO}_2 + 3\text{H}_2\text{SO}_4 \longrightarrow 2\text{NaHSO}_4 + \text{MnSO}_4 + 2\text{H}_2\text{O} + \text{Cl}_2$$

4. Pure chlorine may be obtained by heating dry platinic chloride (PtCl<sub>4</sub>) or gold chloride (AuCl<sub>3</sub>) in a hard glass

$$\begin{array}{l} \text{PtCl}_{4} \xrightarrow{\phantom{0}374^{\circ}\text{C}} \text{PtCl}_{2} + \text{Cl}_{2} \xrightarrow{\phantom{0}582^{\circ}\text{C}} \text{Pt} + 2\text{Cl}_{2} \\ 2\text{AuCl}_{3} \xrightarrow{\phantom{0}175^{\circ}\text{C}} 2\text{AuCl} + 2\text{Cl}_{2} \xrightarrow{\phantom{0}185^{\circ}\text{C}} 2\text{Au} + 3\text{Cl}_{2} \end{array}$$

#### Manufacture of chlorine:

1. Electrolytic process: Chlorine is obtained by the electrolysis of a concentrated solution of NaCl (brine), when Cl2 is liberated at the anode and the sodium metal liberated at the cathode reacts with  $\rm H_2O$  to form NaOH and  $\rm H_2.$ 

At anode: 
$$2Cl^{\Theta} \longrightarrow Cl_2 + 2e^{\Theta}$$

At cathode: 
$$2e^- + 2H_2O \longrightarrow 2OH^{\odot} + H_2(g)$$

(Since the reduction potential of  $H_2O >$  reduction potential of Na, so reduction of H<sub>2</sub>O occurs)

Net reaction:

$$2Cl^{\Theta}(aq) + 2H_2O(l) \longrightarrow 2OH^{\Theta}(aq) + H_2(g) + Cl_2(g)$$

For the given reaction,  $\Delta_r G^{\odot}$  is +422 J.

Therefore, an external e.m.f. more than 2.2 V is required for the extraction of Cl<sub>2</sub> from brine.

It is also obtained as a by product during manufacture of sodium by electrolysis of fused NaCl in Down's process.

2. Weldon's process: It involves the heating of pyrolusite mineral (MnO<sub>2</sub>) with concentrated hydrochloric acid in stone-ware stills.

$$MnO_2 + 4HCl \longrightarrow MnCl_2 + 2H_2O + Cl_2\uparrow$$

The manganese chloride present in the waste liquor is converted into a product which can be used instead of fresh pyrolusite for oxidising more of hydrochloric acid. The manganese chloride solution is mixed with excess of lime and air is blown in the heated mixture. The following changes occur:

$$MnCl_2 + Ca(OH)_2 \longrightarrow Mn(OH)_2 + CaCl_2$$
  
 $2Mn(OH)_2 + O_2 \longrightarrow 2MnO_2 + 2H_2O$   
 $(Air)$   
 $MnO_2 + Ca(OH)_2 \longrightarrow CaMnO_3 + H_2O$   
Calcium manganite

Calcium manganite settles down to the bottom as a dark coloured mud. This is used for oxidation of fresh quantities of hydrochloric acid.

$$CaMnO_3 + 6HCl \longrightarrow CaCl_2 + MnCl_2 + Cl_2 + 3H_2O$$

3. Deacon's process: Deacon's process is superior to Weldon's process. In this process, chlorine is obtained by the oxidation of HCl with air in presence of cupric chloride heated to 400°C.

$$4HCl + O_2 \xrightarrow{CuCl_2} 2Cl_2 + 2H_2O$$

The catalytic action of cupric chloride can be explained with the following mechanism.

$$2CuCl_2 + O_2 \xrightarrow{\text{High temp.}} Cu_2Cl_2 + Cl_2$$

$$2Cu_2Cl_2 + O_2 \xrightarrow{\text{Air}} 2Cu_2Cl_2$$

$$Copper oxychloride$$

$$2Cu_2Cl_2 + 2HCl \xrightarrow{\text{Copper oxychloride}} 2Cu_2Cl_2 + H_2O$$

The cycle is then repeated, the gaseous products being steam and chlorine.

4 Nitrosyl chloride process: In this process, common salt (NaCl) is treated with concentrated nitric acid, when a mixture of chlorine and nitrosyl chloride is evolved.

$$[NaCl + HNO_3 \longrightarrow NaNO_3 + HCl] \times 3$$

$$HNO_3 + 3HCl \longrightarrow NOCl + Cl_2 + 2H_2O$$

$$3$$
NaCl +  $4$ HNO<sub>3</sub>  $\longrightarrow$   $3$ NaNO<sub>3</sub> + NOCl + Cl<sub>2</sub> +  $2$ H<sub>2</sub>O

The gaseous mixture is oxidised with oxygen.

$$2NOC1 + O_2 \longrightarrow 2NO_2 + Cl_2$$

The gases are liquefied and chlorine distilled out. Nitrogen dioxide is absorbed in water in presence of oxygen to form nitric acid which can be used again.

$$4NO_2 + O_2 + 2H_2O \longrightarrow 4HNO_3$$

Nowadays, due to economical reasons, nitrosyl chloride process is used to manufacture chlorine.

Storage and transportation of chlorine: Chlorine is stored and transported in the liquid state. The liquid is stored in large steel tanks which are kept in heat-insulated cold storage rooms.

#### **Properties:**

### (A) Physical properties

1. It is a greenish yellow gas with pungent and suffocating odour.

- 2. It is 2.5 times heavier than air.
- **3.** It can be easily liquefied into greenish yellow liquid which boils at 239 K.
- **4.** It is fairly soluble in water. The aqueous solution is called **chlorine water.** It has yellow colour and smells of chlorine. At 0°C, crystals of chlorine hydrate, Cl<sub>2</sub>·8H<sub>2</sub>O are formed.

## (B) Chemical properties

- 1. Combustibility: Chlorine does not burn and also does not help in burning.
- 2. Reaction with metals, non-metals and metalloids:
  Chlorine reacts with a number of metals, non-metals and metalloids to form their corresponding chlorides. For example,

$$2 \text{ Na} + \text{Cl}_2 \longrightarrow 2 \text{NaCl}; \quad 2 \text{Al} + 3 \text{Cl}_2 \xrightarrow{\Delta} 2 \text{AlCl}_3$$
 $2 \text{B} + 3 \text{Cl}_2 \xrightarrow{\Delta} 2 \text{BCl}_3$ 
 $2 \text{Fe} + 3 \text{Cl}_2 \longrightarrow 2 \text{FeCl}_3; \quad P_4 + 6 \text{Cl}_2 \xrightarrow{\Delta} 4 \text{PCl}_3$ 
 $S_8 + 4 \text{Cl}_2 \xrightarrow{\Delta} 4 S_2 \text{Cl}_2; \quad 2 \text{As} + 3 \text{Cl}_2 \xrightarrow{\Delta} 2 \text{AsCl}_3$ 
It combines with all the non-metals, except  $N_2$ ,  $O_2$ ,  $C$  and inert gases. It combines with  $H_2$  in light (but not in dark) with explosion to form HCl. However, in presence of charcoal as a catalyst, the reaction is safe.

- **3. Affinity for hydrogen:** It has great affinity for hydrogen. It decomposes several hydrogen compounds forming HCl.
  - i. Turpentine burns in chlorine forming HCl and carbon.  $C_{10}H_{16} + 8Cl_2 \longrightarrow 10C + 16HCl$
  - ii. It reacts with water in the presence of sunlight and forms  $\rm O_2$ .

$$2H_2O + 2Cl_2 \longrightarrow 4HCl + O_2$$

- iii. It reacts with ammonia under two conditions:
  - **a.** When ammonia is in excess: The products are nitrogen and ammonium chloride.

$$2NH_3 + 3Cl_2 \longrightarrow N_2 + 3HCl$$

$$[2NH_3 + HCl \longrightarrow NH_4Cl] \times 6$$

$$8NH_3 + 3Cl_2 \longrightarrow N_2 + 6NH_4Cl$$

**b.** When chlorine is in excess: The products are nitrogen trichloride (explosive) and HCl.

$$NH_3 + 3Cl_2 \longrightarrow NCl_3 + 3HCl$$

iv. It removes hydrogen from H<sub>2</sub>S.

$$H_2S + Cl_2 \longrightarrow 2HCl + S$$

4. Oxidising properties: In presence of moisture, Cl<sub>2</sub> acts as an oxidising agent. When Cl<sub>2</sub> is dissolved in water it forms chlorine water. On standing, chlorine water loses its yellow colour due to the formation of HCl and HOCl. Hypochlorous acid (HOCl) thus formed, being unstable, decomposes to give nascent oxygen which is responsible for oxidising properties of chlorine.

$$Cl_2 + H_2O \longrightarrow HCl + HOCl$$
 $HOCl \longrightarrow HCl + [O]$ 
 $Cl_2 + H_2O \longrightarrow 2HCl + [O]$ 

Thus, in presence of moisture or in aqueous solution, () acts as a strong oxidising agent.

a. Oxidises acidified ferrous to ferric salts.

$$Cl_2 + H_2O \longrightarrow 2 \text{ HCl} + [O]$$

$$2\text{FeSO}_4 + H_2\text{SO}_4 + [O] \longrightarrow \text{Fe}_2(\text{SO})_3 + H_2O$$

$$2\text{FeSO}_4 + H_2\text{SO}_4 + Cl_2 \longrightarrow \text{Fe}_2(\text{SO}_4)_3 + 2 \text{ HCl}$$

b. Oxidises sulphites to sulphates.

$$Na_2SO_3 + Cl_2 + H_2O \longrightarrow Na_2SO_4 + 2HCl$$

c. Oxidises thiosulphates to bisulphates

$$Na_2S_2O_3 + 4Cl_2 + 5H_2O \longrightarrow 2NaHSO_4 + 8HC$$
  
Sodium thiosulphate

d. Oxidises sulphur dioxide to sulphuric acid in aqueous solution

$$SO_2 + 2H_2O + Cl_2 \longrightarrow H_2SO_4 + 2HCl$$

e. Oxidises moist iodine to iodic acid.

$$I_2 + 6H_2O + 5CI_2 \longrightarrow 2HIO_3 + 10HCI$$
odine
Iodic acid

**f.** Oxidises H<sub>2</sub>S to S in presence of water.

$$H_2S + Cl_2 \xrightarrow{\text{water}} 2HCl + S$$

g. Oxidises sodium arsenite to sodium arsenate.

$$Na_3AsO_3 + H_2O + Cl_2 \longrightarrow Na_3AsO_4 + 2 HCl$$
  
Sodium arsenite Sodium arsenate

h. Oxidises nitrites to nitrates

$$NaNO_2 + Cl_2 + H_2O \longrightarrow NaNO_3 + 2HCl$$

 Bleaching action: In presence of moisture or in aqueous solution, Cl<sub>2</sub> acts as a powerful bleaching agent and bleaches vegetable or organic matter.

$$Cl_2 + H_2O \longrightarrow 2HCl + [O]$$

Coloured substance  $+ [O] \longrightarrow Colourless$  substance

The bleaching action of  $\operatorname{Cl}_2$  is due to oxidation of coloured substances to colourless substances by nascent oxygen. Since the bleaching action of  $\operatorname{Cl}_2$  is due to oxidation while that of  $\operatorname{SO}_2$  is due to reduction, hence, bleaching effect of  $\operatorname{Cl}_2$  is permanent while that of  $\operatorname{SO}_2$  temporary.

6. Reaction with cold and hot alkalies: When Cl, is passed into cold dilute solution of alkalies, a mixture of chloride and hypochlorite is formed.

$$2\text{NaOH} + \text{Cl}_2 \longrightarrow \text{NaCl} + \text{NaOCl} + \text{H}_2\text{O}$$

$$\text{Sodium} \quad \text{Sodium}$$

$$\text{chloride} \quad \text{hypochlorite}$$

$$2\text{KOH} + \text{Cl}_2 \longrightarrow \text{KCl} + \text{KOCl} + \text{H}_2\text{O}$$

$$2\text{Ca}(\text{OH})_2 + 2\text{Cl}_2 \longrightarrow \text{CaCl}_2 + \text{Ca}(\text{OCl})_2 + 2\text{H}_2\text{O}$$

$$\text{Calcium} \quad \text{Calcium}$$

$$\text{chloride} \quad \text{hypochlorite}$$

However, when Cl<sub>2</sub> is passed through hot and concentrated alkali solution, a mixture of chloride and chlorate is formed.

$$3Cl_{2} + 6NaOH \xrightarrow{Hot} 5NaCl + NaClO_{3} + 3H_{2}O$$
conc.
Sodium Sodium chloride chlorate

$${}^{(0)}_{6\text{Cl}_2} + 6\text{Ca(OH)}_2 \xrightarrow{\text{Hot}} 5\text{CaCl}_2 + \text{Ca(ClO}_3)_2 + 6\text{H}_2^0$$

During these reactions, chlorine is simultaneously reduced to chloride ion,  $Cl^{\Theta}$  and oxidised to either hypochlorite  ${}^{\Theta}OCl)$  or chlorate  $(ClO_3^{\Theta})$  ion. Such reaction which involves simultaneous oxidation—reduction is known as disproportionation reaction.

7. Reaction with dry slaked lime: Chlorine reacts with dry slaked lime to form bleaching powder.

$$\frac{\text{Slaket into}}{2\text{Ca}(\text{OH})_2 + 2\text{Cl}_2} \longrightarrow \frac{\text{Ca}(\text{OCl})_2}{\text{Calcium hypochlorite}} + \frac{\text{CaCl}_2 + 2\text{H}_2\text{O}}{\text{Calcium hypochlorite}}$$

The actual composition of bleaching powder is

Ca(OCl)<sub>2</sub>·CaCl<sub>2</sub>·Ca(OH)<sub>2</sub>·2H<sub>2</sub>O

b. Cl<sub>2</sub> also reacts with many non-metal oxides to form addition products.

$$SO_2 + Cl_2 \longrightarrow SO_2Cl_2$$

(Sulphuryl chloride)

$$2 \text{ NO} + \text{Cl}_2 \longrightarrow 2 \text{ NOC1}$$

(Nitrosyl chloride)

$$CO + Cl_2 \longrightarrow COCl_2(Carbonyl chloride or phosgene)$$

#### Uses:

- For bleaching wood pulp (required for manufacture of paper and rayon), cotton and textiles.
- ii. In the manufacture of dyes, drugs and organic compounds such as CHCl<sub>3</sub>, CCl<sub>4</sub>, DDT, refrigerants (CCl<sub>2</sub>F<sub>2</sub>, freon) and bleaching powder.
- iii. In the metallurgy (extraction) of gold and platinum.
- iv. In sterilising drinking water.
- v. In the preparation of poisonous gases like phosgene (COCl<sub>2</sub>), tear gas (CCl<sub>3</sub>·NO<sub>2</sub>), mustard gas (ClCH<sub>2</sub>CH<sub>2</sub>SCH<sub>2</sub>CH<sub>2</sub>Cl), etc. Mustard gas was used by Germany in World War I.
- vi. As a germicide and disinfectant.

## 4.9 **BROMINE**

Bromine was discovered in 1826 by the French chemist **Balard** in the mother liquor left after the crystallisation of common salt from sea water. The name bromine was given due to its bad and pungent odour (**Greek word**, '**Bromos**', which means 'stench').

## Preparation:

1. By passing chlorine through the solution of potassium or magnesium bromide.

$$2KBr + Cl_2 \longrightarrow 2KCl + Br_2$$

$$MgBr_2 + Cl_2 \longrightarrow MgCl_2 + Br_2$$

2. By adding hydrochloric acid to the mixture containing potassium bromide and potassium bromate.

$$5KBr + KBrO_3 + 6HCl \longrightarrow 6KCl + 3Br_2 + 3H_2O$$

3. By heating mixture of potassium bromide and manganese dioxide with conc. H<sub>2</sub>SO<sub>4</sub>.

$$MnO_2 + H_2SO_4 \longrightarrow MnSO_4 + H_2O + [O]$$

$$[KBr + H_2SO_4 \longrightarrow KHSO_4 + HBr] \times 2$$

$$2HBr + [O] \longrightarrow H_2O + Br_2$$

 $2KBr + MnO<sub>2</sub> + 3H<sub>2</sub>SO<sub>4</sub> \longrightarrow 2KHSO<sub>4</sub> + MnSO<sub>4</sub> + Br<sub>2</sub> + 2H<sub>2</sub>O$ 

This reaction is commonly used in the laboratory for the preparation of bromine  $(Br_2)$ .

#### Manufacture:

 From sea water: Sea water is the most important source of commercial bromine. The sea water is slightly acidified and then treated with chlorine to liberate the bromine.

$$Cl_2$$
 + Bromides  $\longrightarrow$  Chlorides +  $Br_2$   
(Sea water)

The evolved bromine is blown out by means of a current of air. The air carrying the bromine vapours is passed through absorption towers down which a sodium carbonate solution is sprayed. The bromide combines forming sodium bromate and sodium bromide.

$$3\text{Na}_2\text{CO}_3 + 3\text{Br}_2 \longrightarrow \text{NaBrO}_3 + 5\text{NaBr} + 3\text{CO}_2$$

The solution containing bromide and bromate is distilled with H<sub>2</sub>SO<sub>4</sub> to recover bromine.

$$[2NaBr + H_2SO_4 \longrightarrow Na_2SO_4 + 2HBr] \times 5$$

$$2\text{NaBrO}_3 + \text{H}_2\text{SO}_4 \longrightarrow \text{Na}_2\text{SO}_4 + 2\text{HBrO}_3$$

$$[HBrO_3 + 5HBr \longrightarrow 3Br + 3H_2O] \times 2$$

$$\frac{10\text{NaBr} + 2\text{NaBrO}_3 + 6\text{H}_2\text{SO}_4 \longrightarrow 6\text{Na}_2\text{SO}_4 + 6\text{Br}_2 + 6\text{H}_2\text{O}}{6\text{NaBr} + \text{NaBrO}_3 + 3\text{H}_2\text{SO}_4 \longrightarrow 3\text{Na}_2\text{SO}_4 + 3\text{Br}_2 + 3\text{H}_2\text{O}}$$

The vapours are condensed.

2. From carnallite mother liquor: The mother liquor left after the crystallisation of potassium chloride from carnallite contains about 0.25% of bromine as magnesium bromide and potassium bromide and is known as bittern.

The hot mother liquor is made to flow down a tower packed with earthen-ware balls. A current of chlorine and steam is introduced from the bottom of the tower. The vapours of bromine set free are condensed in a condenser.

$$MgBr_2 + Cl_2 \longrightarrow MgCl_2 + Br_2$$

## **Properties:**

## (A) Physical properties

- 1. It is a reddish brown, heavy mobile liquid.
- 2. Its density is 3.2.
- 3. It has irritating bad odour.
- 4. It freezes to give yellowish brown solid.
- **5.** Br<sub>2</sub> vapours attack the eyes and mucous membrane of nose and throat. It brings blisters on the skin which take a very long time to heel. It is highly poisonous.
- **6.** It is fairly soluble in water (3.6% at 20°C). The solution is termed bromine water. A saturated solution of bromine when cooled in a freezing mixture gives Br<sub>2</sub>.8H<sub>2</sub>O.
- It is more soluble in chloroform, carbon tetrachloride, etc. The colour of the solution is usually reddish brown.
- **(B) Chemical properties:** Br<sub>2</sub> closely resembles Cl<sub>2</sub> in its properties.
  - Oxidising properties: Bromine is a good oxidising agent.
    It ordinarily does not react with water but in presence of an
    oxidisable substance forms hydrogen bromide and oxyger
    with water.

$$Br_2 + H_2O \longrightarrow 2HBr + [O]$$
  
  $X + [O] \longrightarrow XO$ 

Oxidisable substance

a. Oxidises SO<sub>2</sub> to sulphuric acid.

$$SO_2 + Br_2 + 2H_2O \longrightarrow 2HBr + H_2SO_4$$

b. Oxidises sulphites to sulphates.

$$Na_2SO_3 + Br_2 + H_2O \longrightarrow Na_2SO_4 + 2HBr$$

c. Oxidises arsenites to arsenates.

$$Na_3AsO_3 + Br_2 + H_2O \longrightarrow Na_3AsO_4 + 2HBr$$

d. Oxidises thiosulphates to sulphate.

$$Na_2S_2O_3 + Br_2 + H_2O \longrightarrow Na_2SO_4 + S + 2HBr$$

e. Sulphur is formed by oxidation of hydrogen sulphide.

$$H_2S + Br_2 \longrightarrow 2HBr + S$$

f. Iodine is liberated from iodides.

$$2KI + Br_2 \longrightarrow 2KBr + I_2$$

2. Reactions with alkalies: The action of bromine on alkalies is similar to that of chlorine, a hypobromite with a cold dilute solution and a bromate with a hot solution are formed.

$$(0) \qquad (-1) \qquad (+1)$$

$$2KOH + Br_2 \longrightarrow KBr + KOBr + 3H_2O$$

$$(dil. and cold) \qquad Potassium \\ hypobromide$$

$$(0) \qquad (-1) \qquad (+5)$$

$$6KOH + 3Br_2 \longrightarrow 5KBr + KBrO_3 + 3H_2O$$

$$(conc. and hot) \qquad Potassium$$

$$6Ba(OH)_2 + 6Br_2 \longrightarrow 5BaBr_2 + Ba(BrO_3)_2 + 6H_2O$$

(Conc. and hot)

Barium bromate

$$3\text{Na}_2\text{CO}_3 + 3\text{Br}_2 \longrightarrow 5\text{NaBr} + \text{NaBrO}_3 + 3\text{CO}_2$$

(Conc. and hot)

However, with slaked lime (dry) it forms a compound similar to bleaching powder.

$$Ca(OH)_2 + Br_2 \longrightarrow CaOBr_2 + H_2O$$
  
Slaked lime  
(Dry)

- 3. Reaction with ammonia: It is similar to that of chlorine.  $8NH_3 + 3Br_2 \longrightarrow 6NH_4Br + N_2$
- 4. Bleaching action: The bleaching action of bromine is weaker than that of chlorine. The bleaching action is due to its oxidising property.

#### Uses:

- i. The chief use of bromine is in the manufacture of ethylene bromide (C<sub>2</sub>H<sub>4</sub>Br<sub>2</sub>) which is extensively employed as a component of anti-knock gasoline.
- ii. In the manufacture of NaBr and KBr (used in medicine as sedative), and certain organic dyes.
- **iii.** Bromine water is used in organic chemistry to test the unsaturation of organic compounds.
- iv. As germicide.
- v. It is used as an oxidising agent and in organic synthesis.

## 4.10 IODINE

Iodine was discovered by **Bernard Courtois** in 1812 from the ashes of sea-weeds. Gay-Lussac established its elementary nature

and named it iodine on account of the violet colour of its Vapollis (Greek word, 'Iodos' which means 'violet').

## **Properties:**

- 1. By passing chlorine through potassium iodide solution,  $2KI + Cl_2 \longrightarrow 2KCl + I_2$
- By adding potassium iodide solution to copper sulphale solution.

$$\begin{array}{c} \text{CuSO}_4 + 2\text{KI} \longrightarrow \text{CuI}_2 + \text{K}_2\text{SO}_4 \\ 2\text{CuI}_2 \longrightarrow \text{Cu}_2\text{I}_2 + \text{I}_2 \\ \text{Cupric iodide} & \text{Cuprous iodide} \end{array}$$

3. By heating mixture of potassium iodide and manganess dioxide with conc. H<sub>2</sub>SO<sub>4</sub>.

$$2KI + 2H_2SO_4 \longrightarrow 2KHSO_4 + 2HI$$
 $MnO_2 + H_2SO_4 \longrightarrow MnSO_4 + H_2O + [O]$ 
 $2HI + [O] \longrightarrow H_2O + I_2$ 
 $2KI + MnO_2 + 3H_2SO_4 \longrightarrow 2KHSO_4 + MnSO_4 + 2H_2O + [O]$ 
In laboratory, iodine is usually prepared by this reaction

## **Properties:**

### (A) Physical properties

- 1. It is a black (dark violet) shining solid, i.e., it has metallic lustre.
- 2. It sublimes rapidly below melting point giving violet coloured vapours.
- 3. Iodine produces stains on skin, its vapours are pungent and irritating and very dangerous to inhale.
- 4. Its specific gravity is 4.98. It is diatomic in nature and when heated at 1700°C, it is converted into atomic form.

$$I_2 = \frac{1700^{\circ}C}{}I + I$$

5. It is slightly soluble in water and gives a light brown solution. Its solubility increases in water in presence of potassium iodide due to the formation of potassium triiodide. KI<sub>3</sub> easily breaks down and thus the solution has all the properties of free iodine.

$$I_2 + KI \longrightarrow KI_3$$

- 6. It is soluble in many organic solvents such as chloroform carbon tetrachloride, alcohol, ether and carbon disulphide. The solution in CS<sub>2</sub>, CHCl<sub>3</sub> and CCl<sub>4</sub> is violet in colour.
- 7. The most notable feature of I<sub>2</sub> solution in organic solvents is the dependence of their colour on the nature of the solvent. The solutions in aliphatic hydrocarbons such as CCl<sub>4</sub> violet and those in stronger donor solvents such as alcohols, ethers or amines is deep brown and those in aromatic hydrocarbons is light brown.

The variation in colour, can be explained in terms of a weak donor–acceptor interaction leading to complex formation between the solvent S (donor) and  $I_2$  (acceptor),  $I_2$ ...S. Such interactions are known as the "charge transfer type and the complexes are known as charge transfer complexes. The violet colour of  $I_2$  vapour is due to an excitation of an electron from  $\pi^* \longrightarrow \sigma^*$  molecular orbital. In non-coordinating solvents, the transition energy is for

 $\pi^* \longrightarrow \sigma^*$  transition and hence the colour remains the same. However, in a donor solvent, the  $\sigma^*$  antibonding molecular orbital of I<sub>2</sub> acts as an electron acceptor and weakens the I-I bond. This alters the transition energy and leads to the appearance of new charge transfer band in then near UV spectrum (230-330 nm).

## (B) Chemical properties

lodine is chemically less reactive than chlorine and bromine.

1. Reaction with alkalies: Iodine reacts with cold dilute solution of NaOH forming hypoiodite. The colour of the solution becomes faint yellow. However, hypoiodite undergoes hydrolysis forming HOI.

$$\begin{split} 2\text{NaOH} + \text{I}_2 &\longrightarrow \text{NaOI} + \text{NaI} + \text{H}_2\text{O} \\ \text{NaOI} + \text{H}_2\text{O} &\longrightarrow \text{NaOH} + \text{HOI} \\ \text{NaOH} + \text{I}_2 &\longrightarrow 4\text{NaI} + \text{HOI} \\ &\qquad \qquad \text{Hypoiodous acid} \end{split}$$

lodine when heated with concentrated alkali solution, iodide and iodate are formed. The colour of iodine disappears.

$$6\text{NaOH} + 3\text{I}_2 \longrightarrow \underbrace{5\text{NaI} + \text{NaIO}_3}_{\text{Colourless}} + 3\text{H}_2\text{O}$$

2. Iodine does not displace chlorine and bromine from chlorides and bromides, respectively but it displaces them from their oxy salts.

$$2\text{KClO}_3 + \text{I}_2 \longrightarrow 2\text{KlO}_3 + \text{Cl}_2$$
$$2\text{KBrO}_3 + \text{I}_2 \longrightarrow 2\text{KlO}_3 + \text{Br}_2$$

3. Reaction with sodium thiosulphate: Iodine solution is decolourised by sodium thiosulphate (hypo) as sodium tetrathionate and sodium iodide are formed. Both are colourless and soluble.

$$2Na_2S_2O_3 + I_2 \longrightarrow 2NaI + Na_2S_4O_6$$
ium thiosulphate Sodium tetrathionate

Sodium thiosulphate

This reaction is involved in iodometric titrations in presence of starch indicator.

4. Reaction with NH<sub>3</sub>: Iodine forms a mild explosive with ammonia.

$$2NH_3 + 3I_2 \longrightarrow NI_3.NH_3 + 3HI$$
Explosive

$$8NI_3.NH_3 \longrightarrow 5N_2 + 9I_2 + 6NH_4I$$

- 5. Reaction with strong oxidising agents: Strong oxidising agents convert iodine to iodic acid (HIO<sub>3</sub>).
  - i. With conc. HNO<sub>3</sub>:

$$I_2 + 10HNO_3 \longrightarrow 2HIO_3 + 10NO_2 + 4H_2O$$

ii. With ozone:

Uses:

$$I_2 + H_2O + 5O_3 \longrightarrow 2HIO_3 + 5O_2$$

iii. With chlorine water:

$$I_2 + 5Cl_2 + 6H_2O \longrightarrow 2HIO_3 + 10HCl$$

i. It is used in medicine, e.g., tincture of iodine [1/2 oz. iodine, 1/4 oz. KI and 1 pint rectified spirit] and iodex as antiseptic and analgesic. Solutions of iodine in KI are used in the treatment of goitre.

- ii. In the preparation of iodoform, iodides, dyes, etc.
- iii. In analytical chemistry.
- iv. In the preparation of photosensitive papers, films and plates.

## 4.11 HALOGEN ACIDS OR HYDRACIDS

All the halogens combine with hydrogen and form covalent hydrides of the type HX, where X = F, Cl, Br and I. These hydrides are known as halogen acids or hydracids.

Halogen acid	HF	HC1	HBr	НІ
Name	Hydrogen	Hydrogen	Hydrogen	Hydrogen
	fluoride	chloride	bromide	iodide

#### Preparation:

Hydrogen fluoride: It is an associated molecule and is represented by formula, H<sub>2</sub>F<sub>2</sub>.

Pure anhydrous hydrogen fluoride is obtained by heating potassium hydrogen fluoride (dry) in a platinum retort.

$$2KHF_2 \longrightarrow KF_2 + H_2F_2$$

The vapours are condensed in a platinum condenser and collected in a platinum receiver. In place of platinum, lead apparatus can also be used.

The aqueous solution of H2F2 can be obtained by heating calcium fluoride with 90% conc. sulphuric acid in a lead retort. Hydrogen chloride:

4. In laboratory, HCl can be prepared by heating a mixture of sodium chloride and conc. H2SO4.

$$NaCl + H_2SO_4 \xrightarrow{420K} NaHSO_4 + HCl$$
  
 $NaHSO_4 + H_2SO_4 \xrightarrow{420K} Na_2SO_4 + HCl$ 

#### Hydrogen bromide:

1. By direct combination of elements: HBr can be prepared by passing a mixture of H, and Br, over a platinum spiral heated to redness by an electric current.

$$H_2 + Br_2 \xrightarrow{Pt} 2HBr$$

2. By heating bromide with conc. orthophosphoric acid.

$$3NaBr + H_3PO_4 \longrightarrow Na_3PO_4 + 3HBr$$

## Hydrogen iodide:

1. HI can be prepared in small quantities by passing hydrogen and iodine vapours over red hot fine platinum.

$$H_2 + I_2 = \frac{Pt}{450^{\circ}C} 2HI$$

2. By heating iodides with conc. orthophosphoric acid.

$$3NaI + H_3PO_4 \longrightarrow Na_3PO_4 + 3HI$$

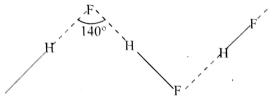
3. By hydrolysis of corresponding phosphorous trihalide.

$$PI_3 + 3H_2O \longrightarrow H_3PO_3 + 3HI$$

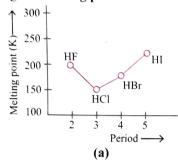
### **Properties:**

1. Physical state: Except hydrogen fluoride, other halogen halides are gases. They fume as air and have pungent odour. These are colourless. All are heavier than air and can be liquefied to colourless liquids.

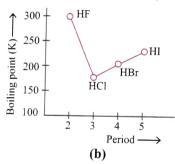
Hydrogen fluoride is a low boiling liquid (b.p. 293 K) The anomalous behaviour of HF is due to the presence of intermolecular hydrogen bonding in its molecules. Consequently, it exists as an associated molecule (HF)<sub>n</sub>. In the solid state, (HF) has the zig-zag structure.



2. a. Melting and boiling points:



[Melting point: HI(222) > HF(190) > HBr(185) > HCl(159) K]



HF(293) > HI(283) > HBr(206) > HCl(189) K

Fig. 4.1 (a) and (b) Melting and boiling points of hydrides of group 17

Explanation of m.pt. and	b.pt. of hydrides of group 17
Melting point	Boiling point
The melting point of HF is slightly lower than that of HI, due to increased molecular mass of HI which increases the van der Waals forces of attraction.  OR  H-Bonding in HF is weaker in the solid state than in liquid or gaseous state.	The boiling point of HF is highest as usual due to the strong H-bonding of HF in the liquid or gaseous state than in the solid state.

## b. Comparison of the melting point and boiling point of NH<sub>3</sub>, H<sub>2</sub>O and HF:

Melting point	Boiling point		
H <sub>2</sub> O (273) > NH <sub>3</sub> (195.2) > HF (190) K	H <sub>2</sub> O (373) > HF (293) > NH <sub>3</sub> (238.5) K		

ENofF>O>N,SO,HF should have stronger H-bonding. But both  $\rm H_2O$  and  $\rm NH_3$  form four H-bonding while HF forms only two H-bonding. Moreover, the H-bonding in  $\rm NH_3$  is stronger in the solid state than in the liquid or gaseous state. Whereas the H-bond in HF is weaker in the solid state than in the liquid or gaseous state. Hence the m. pt. of  $\rm H_2O>NH_3>HF$  as given above.

Both  $H_2O$  and  $NH_3$  form four H-bonding while HF forms only two H-bonding. But H-bonding of HF in the liquid or gaseous state is stronger than in solid state. Therefore, the boiling point of HF > b.pt. of  $NH_3$ . Hence, the boiling point of  $H_2O$  > HF >  $NH_3$  as given above.

c. Existence of KHF<sub>2</sub> and non-existence of KHCl<sub>2</sub> KHBr<sub>2</sub> or KHI<sub>2</sub> (dissociation): In aqueous solution HF dissociates and gives the hydrogen diffuoride in (HF<sub>2</sub>) HF. This explains the existence of KHF<sub>2</sub>.

 $H-F + H_2O$   $H_3O^{\oplus}-F^{\ominus}$  (does not occur)  $H_2O \longrightarrow HF_2^{\ominus} + H_3O$ (it occurs)

Whereas due to not so high electronegativity and large size of Cl, Br and I, the molecules of HCl, HBr and HI do not form H-bonding. This explains the non-existence of compounds such as KHCl<sub>2</sub>. KHBr and KHI<sub>2</sub>.

3. Dipole moment: With the increase in electronegativity of halogens down the group (↓), the dipole moment of the hydrogen halides decreases
Dipole moment (μ): HF > HCl > HBr > HI

4. Constant boiling mixture: They are fairly soluble in water and form constant boiling mixtures with water called azeotrope.

 Halogen acid
 HF
 HCl
 HBr
 HI

 Composition
 36%
 20.4%
 47%
 57%

 Boiling point (°C)
 120
 110
 126
 127

5. Ionic character: Down the group (↓), with the decrease in electronegativity of halogen, the dipole moment of the halogen acid and hence the ionic character decreases.

% Ionic character: HF > HCl > HBr > HI

**6. Bond length:** With the increase in size of halogen atom, the bond length increases.

Bond length: HF < HCl < HBr < HI

7. Stability or bond strength: Bond strength is inversely proportional to bond length. Hence, with the increase in bond length, bond strength decreases down the group (↓)

Bond strength: HF > HCl > HBr > HI

With the increase in bond length or with decrease in bond strength, bond dissociation enthalpy decreases.

Bond-dissociation enthalpy: HF > HCl > HBr > HI

8. Thermal stability: Thermal stability is directly proportional to the bond dissociation enthalpy. Since bond dissociation

enthalpy of HF is the highest and that of HI is the least, therefore, HF is the most stable halogen acid while HI is the least stable halogen acid.

Thermal stability: HF > HCl > HBr > HI

 Acid strength: Hydrogen halides in the gaseous state are essentially covalent. In aqueous solution, however, they ionise and act as acids.

Thus, higher the bond dissociation enthalpy, lower is the degree of ionisation and hence weaker is the acid. Since the bond dissociation enthalpies of the halogen acids increase in the order: HI < HBr < HCI < HF, therefore, strength of the acids increases in the reverse direction, i.e., HF < HC1 < HBr < HI.

Another reason for low acidity of HF as compared to other halogen acids is the strong H-bonding of  $F^{\ominus}$  ion to  $H_3O^{\oplus}$  as compared to other halide ions.

10. Reducing nature: The reducing nature of a halogen acid depends upon the ease with which it decomposes to give H, and X<sub>2</sub>.

$$2HX \longrightarrow H_2 + X_2$$

This, in turn, depends upon the bond dissociation enthalpy. Thus, greater the bond dissociation energy, more stable is the halogen acid and hence weaker is the reducing agent. Since the bond dissociation enthalpies of the halogen acids increase in the order: HI < HBr < HC1 < HF, therefore, reducing nature of halogen acids increases in the reverse order: HF < HC1 < HBr < HI.

HF does not show any reducing nature. It cannot be oxidised even by strong oxidising agents. HI is the strongest reducing agent. Its aqueous solution gets oxidised even by atmospheric oxygen.

HCl can be oxidised by strong oxidising agents like

 $\mathrm{MnO}_2$ ,  $\mathrm{KMnO}_4$ ,  $\mathrm{K}_2\mathrm{Cr}_2\mathrm{O}_7$ ,  $\mathrm{PbO}_2$ ,  $\mathrm{Pb}_3\mathrm{O}_4$  etc.

HBr acts as stronger reducing agent than HCl. It can be oxidised by  $\rm H_2SO_4$  and atmospheric oxygen.

HI is the strongest reducing agent.

It reduces  $H_2SO_4$  to  $SO_2$ , S to  $H_2S$ , nitric acid to  $NO_2$ , nitrous acid to NO,  $FeCl_3$  to  $FeCl_2$ , cupric salt to cuprous salt, etc.

11. Action of halogens: F<sub>2</sub> can displace Cl<sub>2</sub>, Br<sub>2</sub> and I<sub>2</sub> from HCl, HBr and HI.

2HCI + 
$$F_2 \longrightarrow$$
 2HF + Cl<sub>2</sub> 2HBr +  $F_2 \longrightarrow$  2HF + Br<sub>2</sub>  
2HI +  $F_2 \longrightarrow$  2HF + I<sub>2</sub>

 ${\rm Cl_2}$  can displace  ${\rm Br_2}$  and  ${\rm I_2}$  from HBr and HI and  ${\rm Br_2}$  can displace only  ${\rm I_2}$  from HI. Iodine can displace none.

12. Reaction with ammonia: HCl, HBr and HI combine with ammonia giving white fumes of ammonium halides.

$$NH_3 + HCl \longrightarrow NH_4Cl$$
  
 $NH_4 + HBr \longrightarrow NH_4Br$ 

(Ammonium chloride)

 $NH_3 + HBr \longrightarrow NH_4Br$  (Ammonium bromide)

 $NH_3 + HI \longrightarrow NH_4I$  (Ammonium iodide)

13. Corrosive nature: All the halogen acids, in particular, HF are corrosive and hence extreme care should be taken while working with them. Out of all the hydrohalic acids,

HF attacks glass and hence etching glass and manufacture of glass shell for television tubes.

## ILLUSTRATION 4.3

- a. Write the balanced chemical equation for the reaction of Cl<sub>2</sub> with hot and concentrated NaOH. Is this reaction a disproportionation reaction?
- **b.** When HCl reacts with finely powdered iron, it forms ferrous chloride and not ferric chloride. Why?
- **c.** Deduce the molecular shape of BrF<sub>3</sub> on the basis of VSEPR theory.

### Sol.

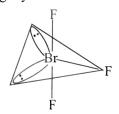
- a. 3Cl<sub>2</sub> + 6NaOH → 5NaCl + NaClO<sub>3</sub> + 3H<sub>2</sub>O

  Yes, chlorine from zero oxidation state is reduced to −1 and oxidised to +3 oxidation states.
- **b.** HCl reacts with Fe to produce H<sub>2</sub> gas.

$$Fe + 2HCl \longrightarrow FeCl_2 + H_2$$

Liberation of H<sub>2</sub> prevents the formation of ferric chloride, FeCl<sub>3</sub>.

c. The central atom Br in BrF<sub>3</sub> has seven electrons in the valence shell. Three of these will form electron pair bonds with three fluorine atoms leaving behind four electrons. Thus, there are three bond pairs and two lone pairs. According to VSEPR theory, these will occupy the corners of trigonal bipyramid. The two lone pairs will occupy the equatorial positions to minimise lone pair and the bond pair—lone pair repulsions which are greater than the bond pair—bond pair repulsions. In addition, the axial fluorine atoms will be bent towards the equatorial fluorine in order to minimise the lone pair—lone pair repulsions. The shape would be of slightly bent T.



## ILLUSTRATION 4.4

Explain the following:

- a. In the preparation of HI from KI, phosphoric acid is preferred to sulphuric acid.
- b. Boiling point of HCl is lower than HF.
- c. Bleaching powder loses its bleaching property when kept in an open bottle for a long time.

#### Sol.

a. Besides acidic nature of sulphuric acid, it acts as an oxidising agent. H<sub>2</sub>SO<sub>4</sub> oxidises HI (reducing agent) formed from KI into iodine. Thus, H<sub>3</sub>PO<sub>4</sub> is preferred as it does not oxidise HI.

$$2KI + 2H_2SO_4 \longrightarrow 2KHSO_4 + 2HI$$
  
 $H_2SO_4 + 2HI \longrightarrow I_2 + SO_2 + 2H_2O$ 

- **b.** In HF, there is hydrogen bonding. It is, therefore, an associated liquid. No hydrogen bonding is present in HCl. Only van der Waals' forces are present. This is the reason why boiling point of HCl is lower than HF.
- c. Bleaching action of bleaching powder is due to release of Cl<sub>2</sub> at the time of application. Chlorine is lost by bleaching powder on long standing in open by the following two processes.
  - i.  $CaOCl_2 + CO_2(air) \longrightarrow CaCO_3 + Cl_2$
  - ii.  $6CaOCl_2 \longrightarrow 5CaCl + Ca(ClO_3)_2$

Thus, CaCl<sub>2</sub> and Ca(ClO<sub>3</sub>)<sub>2</sub> do not release Cl<sub>2</sub> at the time of use. Hence, bleaching property is lost by bleaching powder on exposure for long time.

## 4.12 OXIDES OF FLUORINE

Fluorine forms two binary compounds with oxygen, i.e.

OF,

Oxygen difluoride

 $O_{5}F_{5}$ 

Dioxygen difluoride

 $OF_2$  is thermally stable at 298 K while  $O_2F_2$  is highly unstable and decomposes into its elements even at 178 K.

**Preparation:** Oxygen difluoride  $(OF_2)$  is prepared by passing  $F_2$  through 2% NaOH solution while  $O_2F_2$  (dioxygen difluoride) is obtained by passing electric discharge through a mixture of  $F_2$  and  $O_2$  under low pressure and at liquid air temperature.

$$2F_2 + 2NaOH \longrightarrow 2NaF + H_2O + OF_2$$

$$F_2 + O_2 \xrightarrow{\text{Electric discharge}} O_2 F_2$$

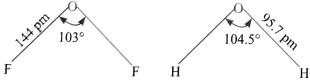
liq. air temp., low pressure

Dioxygen difluoride

OF<sub>2</sub> dissolves in water and gives a neutral solution, therefore, it is not an acid anhydride. It dissolves in NaOH to give sodium fluoride and dioxygen.

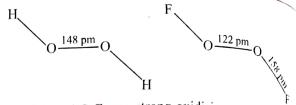
$$2\text{NaOH} + \text{OF}_2 \longrightarrow 2\text{NaF} + \text{H}_2\text{O} + \text{O}_2$$

**Structure:** The structure of  $OF_2$  is similar to that of  $H_2O$  while that of  $O_2F_2$  is similar to that of  $H_2O_2$  involving  $SP^3$  hybridisation of O-atoms. However, due to greater electronegativity of fluorine as compared to oxygen, the bond pairs in  $OF_2$  lie nearer to the fluorine atom.



In contrast, in  $\rm H_2O$ , due to greater electronegativity of O as compared to H, the bond pairs lie nearer the O atom. Consequently, bond pair-bond pair repulsion in  $\rm H_2O$  is more than bond pair-bond pair repulsion in  $\rm OF_2$  and hence F—O—F bond angle is less (103°) than H—O—H bond angle (104.5°).

Further, as F is more electronegative than O, it attracts the lone pairs of electrons on the O atom towards itself. Therefore, lone pair–lone pair repulsion between the two O atoms in O—O bond is much lower in  $O_2F_2$  than in  $H_2O_2$ . In other words, the O—O bond length in  $O_2F_2$  is much shorter (122 pm) than that in  $H_2O_2$  (148 pm). However, the O—F bond lengths in  $O_2F_2$  are much longer (158 pm) than in  $O_2F_2$  (141 pm).



**Uses:** Both  $OF_2$  and  $O_2F_2$  are strong oxidising and fluorinaling agents.  $O_2F_2$  oxidises plutonium (Pu) to  $PuF_6$  and this  $reaction_{||}$  used in removing Pu as  $PuF_6$  from spent nuclear fuel.

$$H_2S + 4O_2F_2 \longrightarrow SF_6 + 2HF + 4O_2$$

Being a strong oxidising agent, OF<sub>2</sub> has been used as a rocket file!

## 4.13 OXIDES OF CHLORINE

Oxidation state	Oxide of chloride	Name
+1	Cl <sub>2</sub> O	Dichlorine monoxide
+4	ClO <sub>2</sub>	Chlorine dioxide
+6	Cl <sub>2</sub> O <sub>6</sub>	Chlorine hexoxide
+7	Cl <sub>2</sub> O <sub>7</sub>	Chlorine heptoxide

## 4.13.1 CHLORINE MONOXIDE, Cl<sub>2</sub>O

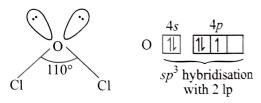
### Preparation:

1. By passing dry Cl<sub>2</sub> (diluted with dry air) over freship precipitated yellow oxide of Hg, i.e., HgO, previoush ignited to 300–400°C and contained in a cooled tube.

$$2$$
HgO +  $2$ Cl<sub>2</sub>  $\longrightarrow$  HgCl<sub>2</sub>.HgO + Cl<sub>2</sub>O

2. By distilling an aqueous solution of hypochlorous active (HOCl) at reduced pressure.

$$2HOCl \longrightarrow H_2O + Cl_2O$$



Geometry: Tetrahedral,

Shape: Bent or V-shaped molecule.

#### **Properties:**

- 1. Brownish yellow gas which condenses to orange coloured liquid (boiling point 273 K).
- 2. It dissolves in water, giving a golden yellow solution of hypochlorous acid. It is therefore, also known anhydride of HOCl. Solubility of Cl<sub>2</sub>O in H<sub>2</sub>O is very high (14.4 g/100 g of H<sub>2</sub>O at -9°C).

$$Cl_2O + H_2O \Longrightarrow 2HOCl$$

3. It acts as strong oxidising agent, which is decomposed to HCl, or oxidises HCl to Cl.

$$Cl_2O + 2HCl \longrightarrow 2Cl_2 + H_2O$$

4.  $Cl_2O$  explodes in the presence of reducing agents of NH<sub>3</sub>  $3Cl_2O + 10NH_3 \longrightarrow 6NH_4Cl + 3H_2O$ 

1. For bleaching highest grade paper pulp. Uses:

2. In water purification and for odour control.

3. In making wool unshrinkable.

3. In the for improving the quality of low grade fats and oils.

## 4.13.2 CHLORINE DIOXIDE, CIO,

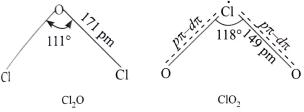
## <sub>preparation:</sub>

From metal chlorater by reacting with oxalic acid.

$$\frac{\text{From metal chioracti by featuring with oxalic acid.}}{\text{gClO}_3 + 2\text{H}_2\text{C}_2\text{O}_4} \xrightarrow{\text{H}_2\text{O}} 2\text{ClO}_2 + 2\text{CO}_2 + \text{K}_2\text{C}_2\text{O}_4 + 2\text{H}_2\text{O}_2\text{O}_4}$$

Advantage of this method: CO<sub>2</sub> formed acts as diluent for the affemely explosive ClO<sub>2</sub> and thus this method is safest method for laboratory preparation of ClO<sub>2</sub>.

Structures: In ClO<sub>2</sub>, the central Cl atom is sp<sup>2</sup>-hybridised with O-Cl—O angle of 118°. Both the Cl—O bonds have equal (149) bond lengths and are quite shorter than those in Cl<sub>2</sub>O (171 Therefore Cl—O bond has appreciable double bond character the to  $p\pi$ - $d\pi$  bonding. The molecule is paramagnetic since it has one odd electron in a p-orbital.



Odd electron molecules often dimerise in order to pair the electrons but ClO2 does not. This is probably due to the reason that odd electron is delocalised. In contrast, the odd electron on N in NO is localised and hence NO readily dimerises to form (NO)2.

#### Properties:

- 1. Dark yellow pungent smelling gas which can be condensed to dark red liquid, boiling point 284 K and frozen to yield orange-red crystals (at 194 K).
- 2. Liquids and gas are fairly stable in dark, but decompose in light. The gas or liquid explodes violently on heating (> -40°C) giving a mixture of Cl<sub>2</sub>, O<sub>2</sub>, Cl<sub>2</sub>O<sub>6</sub> and Cl<sub>2</sub>O.
- 3. It reacts with water to give a mixture of chlorous acid and chloric acid.

$$(+4) \qquad (+3) \qquad (+5) \\ 2\text{ClO}_2 + \text{H}_2\text{O} \longrightarrow \text{HClO}_2 + \text{HClO}_3 \text{ (Disproportionation)} \\ \text{chlorous acid chloric acid.}$$

4. It dissolves in alkali forming chlorite and a chlorate, e.g.

$$\begin{array}{ccc} \text{2ClO}_2 + 2\text{KOH} & \longrightarrow \text{KClO}_2 & + & \text{KClO}_3 + \text{H}_2\text{O} \\ & \text{Potassium} & \text{Potassium} \\ & \text{chlorite} & \text{chlorate} \end{array}$$

5. It acts as powerful oxidising agent and bleaching agent.

$$ClO_2 + 4H^{\oplus} + 5e^{\Theta} \longrightarrow Cl^{\Theta} + 2H_2O \qquad E^{\circ} = +1.50 \text{ V}$$

6. With  $O_3$ :  $2ClO_2 + 2O_3 \xrightarrow{0^{\circ}C} Cl_2O_6 + 2O_2$ 

## <sup>4.13.3</sup> CHLORINE HEXOXIDE, $Cl_2O_6$ ( $Cl_2O_6 \rightleftharpoons 2ClO_3$ )

## Preparation:

Reaction of ozone with ClO<sub>2</sub> at 0°C.

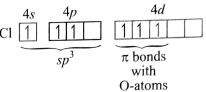
$$2\text{ClO}_2 + 2\text{O}_3 \xrightarrow{\text{0°C}} \text{Cl}_2\text{O}_6 + 2\text{O}_2$$

## Properties and structure:

1. Cl<sub>2</sub>O<sub>6</sub> appears to dissociate to monomer under certain conditions.

$$Cl_2O_6 \stackrel{\Delta}{\Longleftrightarrow} 2ClO_3$$

Pure liquid is diamagnetic, suggesting that most of the species present are Cl<sub>2</sub>O<sub>6</sub> molecules. Vapour, however, is paramagnetic indicating the formation of monomer, ClO<sub>3</sub>.



- 2. It is red, explosive, oily liquid which freezes at 276.5 K. It dissociates on heating and eventually breaks to elements.
- 3. It reacts violently with water, but with cooled water vapour, HClO<sub>4</sub>·H<sub>2</sub>O and HClO<sub>3</sub> are produced.

(+6) (+7) 
$$\text{Cl}_2\text{O}_6 + 2\text{H}_2\text{O} \longrightarrow \text{HClO}_4 \cdot \text{H}_2\text{O} + \text{HClO}_3.$$
 Perchloric acid monohydrate

(Disproportionation)

That is, it is a mixed anhydride of perchloric acid and chloric

4. It dissolves in alkali forming chlorate and perchlorate.

(+6) (+5) (+7)
$$Cl_2O_6 + 2KOH \longrightarrow KClO_3 + KClO_4 + H_2O$$
Potassium Potassium
chlorate perchlorate

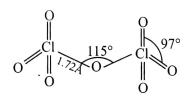
- 5. It is a strong oxidising agent and explodes in contact with grease.
- **6.** With HF:  $Cl_2O_6 + HF \rightleftharpoons HClO_4 + ClO_2F$
- 7. With  $N_2O_4$ :  $Cl_2O_6 + N_2O_4 \rightleftharpoons ClO_2 + [NO_2]^{\oplus} [ClO_4]^{\ominus}$
- **8.** In solid state  $Cl_2O_6$  exist as  $[ClO_2]^{\oplus}$   $[ClO_4]^{\ominus}$  $sp^2 (< 120^\circ)$   $sp^3 (109^\circ, 28')$

## 4.13.4 CHLORINE HEPTOXIDE, $Cl_2O_7$

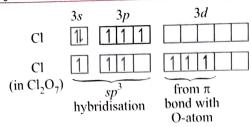
### Preparation:

1. By dehydration of perchloric acid with P<sub>4</sub>O<sub>10</sub> at 263 K.  $4HClO_4 + P_4O_{10} \longrightarrow 2Cl_2O_7 + 4HPO_3$ Cl<sub>2</sub>O<sub>7</sub> may be distilled off under reduced pressure, with precaution against explosions.

#### Structure:



Molecule 3d is polar,  $\mu = 0.72$ 



#### **Properties:**

- 1. It is a colourless, oily liquid (boiling point 355 K) which is extremely explosive in nature. It explodes on heating or on percussion.
- 2. It is moderately stable liquid.
- Slowly reacts with water forming HClO<sub>4</sub> i.e. it is perchloric anhydride.

$$(+6) \qquad (+7)$$

$$Cl_2O_6 + H_2O \longrightarrow 2HClO_4$$

## 4.14 OXIDES OF BROMINE

The bromine oxides Br<sub>2</sub>O, BrO<sub>2</sub> and BrO<sub>3</sub> are the least stable halogen oxides (middle row anomally) and exist only at low temperatures. They are very powerful oxidising agents. Their structures are similar to those of chlorine oxides having comparable molecular formulae.

 $\mathbf{Br_2O}$  is a dark brown solid, moderately stable at 213 K. It is highly oxidising and converts  $I_2$  to  $I_2O_5$ , benzene to 1,4-diquinone.

**Br<sub>2</sub>O** is a pale yellow crystalline solid, which is stable only at < 233 K and decomposes violently into its elements at 273 K. On alkaline, hydrolysis gives bromide and bromate.

$$6BrO_2 + 6OH^{\bigcirc} \longrightarrow 5BrO_3^{\bigcirc} + Br^{\bigcirc} + 3H_2O$$

**BrO**<sub>3</sub> is obtained when Br<sub>2</sub> is treated with O<sub>3</sub> at 273 K. BrO<sub>3</sub> is a white solid which is unstable above 193 K.

## 4.15 OXIDES OF IODINE

Iodine forms three oxides,  $I_2O_4$ ,  $I_2O_5$  and  $I_4O_9$ . Out of these,  $I_2O_5$  is the most stable. It is the only true oxide of iodine while others are regarded as iodates of tripositive iodine, i.e.,  $I_2O_4$  is probably  $[IO]^{\oplus}$   $[IO_3]^{\ominus}$  and  $I_4O_9$  is probably  $I^{3+}(IO_3^{\ominus})_3$ .

**Preparation:**  $I_2O_5$  is obtained by dehydrating iodic acid at 473 K. 2HIO<sub>3</sub>  $\xrightarrow{473\text{K}}$   $I_2O_5 + H_2O$ 

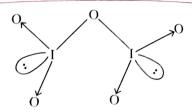
Therefore, it is the anhydride of iodic acid. It dissolves in water to produce iodic acid.

It is a strong oxidising agent and oxidises CO to  $\mathrm{CO}_2$  rapidly and quantitatively at room temperature, liberating  $\mathrm{I}_2$  which can be titrated against a standard solution of  $\mathrm{Na}_2\mathrm{S}_2\mathrm{O}_3$  using starch as an indicator.

$$I_2O_5 + 5CO \xrightarrow{\text{Room temp.}} I_2 + 5CO_2$$

Therefore, I<sub>2</sub>O<sub>5</sub> is used for detection and estimation of CO in the atmosphere and other gaseous mixtures.

**Structure:**  $I_2O_5$  consists of two  $IO_3$  pyramidal units joined through a common oxygen atom. Each iodine has two  $I \to O$  coordinate bonds, one I—O covalent bond and a lone pair of electrons.



## 4.16 OXOACIDS OF HALOGENS

Due to high electronegativity and small size, fluorine forms only one oxoacid, HOF known as fluoric (I) acid or hypofluorous acid. Chlorine, bromine and iodine form four series of oxoacids with formula HOX [halic (I) acid or hypohalous acid], HOXO [halic (III) acid or halous acid], HOXO<sub>2</sub> [halic (V) acid or halic acid] and HOXO<sub>3</sub> [halic (VII) acid or perhalic acid], although many of these are known only in solution or as salts. The names of some important oxoacids along with their oxidation states are given in Table 4.2.

Table 4.2 Oxoacids of halogens

Name / oxidation state	oxidation		Bromine	lodine
Halic (I) acid (Hypo- halous acid)	cid (Hypo- Hypo- fluorous ous		HOBr (Hypobro- mous) acid	HOI (Hypoio- dous) acid
Halic(III) acid (Halous acid)	-	HClO <sub>2</sub> (Chlorous acid)		-
Halic(V) acid (Halic acid)	<del>-</del>	HClO <sub>3</sub> (Chloric acid)	or HBrO <sub>3</sub> (Bromic acid)	HIO <sub>3</sub> (Iodic acid)
Halic(VII) acid (Perhalic acid)	- 1 -	HClO <sub>4</sub> (Perchloric acid)	HBrO <sub>4</sub> (Perbromic acid)	HIO <sub>4</sub> (Periodic acid)

## Acid strength and oxidising power of oxoacids of halogens:

 a. Acid strength of hypohalous acids: Acid strength of oxoacids of different halogens having same oxidation state decreases with the increase in atomic number. or decrease in electronegativity of the halogen.

e.g., 
$$HOC1 > HOBr > HOI$$

electronegativity of the halogen atom. Oxygen is more electronegative than the halogen (Cl, Br or I), therefore, it attracts the electrons of the oxygen-halogen bond towards itself. Now, as the electronegativity of the halogen decreases from Cl to I, the shared pair of electrons of the oxygen-halogen bond moves closer and closer towards the oxygen atom. Consequently, electron-density on the oxygen atom increases from Cl to I. In other words, O atom in H—O—Cl has the lowest electron density while it has the highest in H—O—I

Consequently, O in H—O—Cl attracts the electrons of O—H bond towards itself most strongly followed by in H—O—Br and least strongly in H—O—I. As a result, O—H breaks most readily in H—O—Cl and least easily in H—O—I. In other words, the acid strength of the hypohalous acids decreases in the order:

$$H \leftarrow O \leftarrow Cl > H \rightarrow O \leftarrow Br > H \rightarrow O \rightarrow I$$

b. Oxidising power of hypohalous acids: As the size of the halogen increases, the thermal stability of the O—X bond increases and the oxidising power of the hypohalous acid or the hypohalite ion decreases. Thus, hypochlorites are stronger oxidising agents than hypoiodites. Surprisingly, hypobromite ions and hypochlorite ions are equally strong oxidising agents. This is supported by their electrode potentials:

$$C1 + 2H^{\oplus} + e^{\ominus} \longrightarrow 1/2CI_2 + H_2O; \qquad E^{\circ} = +1.61V$$

$$\Theta_{OBr} + 2H^{\oplus} + e^{\ominus} \longrightarrow 1/2Br_2 + H_2O; \qquad E^{\circ} = +1.60V$$

$$\Theta_{OI} + 2H^{\oplus} + e^{\ominus} \longrightarrow 1/2I_2 + H_2O \qquad E^{\circ} = +1.44V$$

- a. Acid strength of perhalic acids: As the electronegativity of the halogen decreases, the tendency of the XO<sub>3</sub> group to withdraw electrons of the O—H bond towards itself decreases and hence the acid strength of the perhalic acid decreases in the same order, i.e., HClO<sub>4</sub> > HBrO<sub>4</sub> > HIO.
- b. Oxidising power of perhalates: Perhalates are strong oxidising agents, their oxidising power decreases in the order:  $\text{BrO}_4^{\ \ominus} > \text{IO}_4^{\ \ominus} > \text{ClO}_4^{\ \ominus}$

**Explanation:** This order can be explained on the basis of their electrode potentials for the following reactions, i.e.

BrO<sub>4</sub> 
$$^{\ominus}$$
 + 2H $^{\oplus}$  + 2 $e^{\ominus}$   $\longrightarrow$  BrO<sub>3</sub>  $^{\ominus}$  + H<sub>2</sub>O; E° = 1.74 V  
IO<sub>4</sub>  $^{\ominus}$  + 2H $^{\oplus}$  + 2 $e^{\ominus}$   $\longrightarrow$  IO + H<sub>2</sub>O; E° = 1.65 V  
ClO<sub>4</sub>  $^{\ominus}$  + 2H $^{\oplus}$  + 2 $e^{\ominus}$   $\longrightarrow$  ClO<sub>3</sub>  $^{\ominus}$  + H<sub>2</sub>O; E° = 1.19 V  
Although among perhalates, BrO<sub>4</sub>  $^{\ominus}$  is the strongest oxidising agent, yet it is a weaker oxidising agent than F<sub>2</sub>. It is because of this reason that perbromates and perbromic acid can be obtained by oxidation of bromates (Br<sub>3</sub>  $^{\ominus}$ ) by F<sub>2</sub> in alkaline solution.

(Br<sub>3</sub><sup>$$\odot$$</sup>) by F<sub>2</sub> in alkaline solution.  
BrO<sub>3</sub> <sup>$\odot$</sup>  + F<sub>2</sub> + 2OH <sup>$\odot$</sup>   $\longrightarrow$  BrO<sub>4</sub> <sup>$\odot$</sup>  + 2F <sup>$\odot$</sup>  + H<sub>2</sub>O

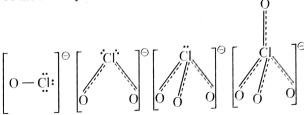
3. Acid strength of oxoacids of the same halogen in different oxidation states: Acid strength of oxoacids of the same halogen increases with increase in oxidation number of the halogen, e.g.,

Acid 
$$HClO_4 > HClO_3 > HClO > HOCl$$
  
 $pK_a = -10 = -1.2 = 2.0 = 7.5$ 

**Explanation:** This can be explained on the basis of the relative stability of the anion (or the conjugate base) left after removal of a proton.

$$\text{HClO}_n + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^{\oplus} + \text{ClO}_n^{\ominus}$$
  
Oxoacid Anion  
 $(n = 1 - 4)$  (Conjugate base)

Now greater the number of oxygen atoms in the anion (conjugate base), greater will be the dispersal of the negative charge through  $p\pi-d\pi$  back bonding and hence greater will be the stability of the anion.



Stability of the ion increases

Since the stability of the anions decreases in the order:  $CIO_4$   $^{\odot}$  >  $CIO_3$   $^{\odot}$  >  $CIO_2$   $^{\odot}$  >  $CIO_2$   $^{\odot}$ 

Hence, their acid strength also decreases in the same order:  $HClO_4 > HClO_3 > HClO_2 > HOCl$ 

Further, as the stability of the anion increases, its oxidising power decreases accordingly. In other words, the oxidising power of the oxoacids of chlorine increases in the reverse order of their acid strength,

i.e., 
$$HClO_4 < HClO_3 < HClO_2 < HOCl$$

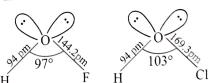
## 4.16.1 Hypofluorous Acid, HOF

Preparation: By fluorination of ice

$$F_2 + H_2O(ice) \stackrel{233K}{\longleftarrow} HOF + HF$$

HOF thus prepared is immediately removed from the reaction mixture otherwise it will be decomposed by HF,  $F_2$  or  $H_2O$ .

**Structure:** In HOF, oxidation state of F is +1. The oxygen atom in HOF like that in HOCl is  $sp^3$ -hybridised. However, due to higher electronegativity of F over Cl, the bond pair–bond pair repulsions of H–O and O–F bonds in HOF are less than those of H–O and O–Cl bonds in HOCl.



Consequently, bond angle in HOF is less than HOCl. As expected due to bigger size of Cl over F, the O—Cl bond is much longer than the O—F bond. But the O—H bonds in both these molecules have approximately the same length.

## **Properties:**

1. HOF is highly unstable and rapidly decomposes at room temperature to form HF and O<sub>2</sub> with a half life of 9.30 minutes.

$$2HOF \longrightarrow 2HF + O_2$$

2. It reacts with H<sub>2</sub>O to form HF and H<sub>2</sub>O<sub>2</sub>.

$$HOF + H_2O \longrightarrow H_2O_2 + HF$$

In other words, it does not ionise in water and hence the corresponding salts, i.e., hypofluorite ions ( ${}^{\bigcirc}$ OF) are not known.

$$HOF + H_2O \longrightarrow H_3O^{\oplus} + {}^{\Theta}OF$$

**3.** HOF cannot be dehydrated to form OF<sub>2</sub>, hence, OF<sub>2</sub> cannot be regarded as an anhydride of HOF. However, HOF reacts with F<sub>2</sub> in presence of H<sub>2</sub>O to form OF<sub>2</sub>.

$$HOF + F_2 \xrightarrow{Aq} HF + O_2$$

**4.** HOF reacts with HF to form  $H_2O + F_2$ HOF + HF  $\longrightarrow$   $H_2O + F_2$ 

## 4.16.2 OXOACIDS OF CHLORINE

Oxidation State	Oxide of chloride	Name
+1	HOCI	Hypochlorous acid
+3	HOCl,	Chlorous acid
+5	HClO <sub>3</sub>	Chloric acid
+7	HClO <sub>4</sub>	Perchloric acid

## 4.16.2.1 Hypochlorous Acid (HOCI)

#### Preparation:

1. By passing Cl<sub>2</sub> gas into water

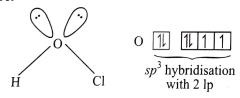
$$\begin{array}{ccc}
(0) & (-1) & (+1) \\
Cl_2 + H_2O \longrightarrow HCl + HOCl
\end{array}$$

2. By shaking  $Cl_2$  water with freshly precipitated yellow HgO.  $2HgO + 2Cl_2 + H_2O \longrightarrow HgCl_2 \cdot HgO \downarrow + 2HOCl$ 

CaCO<sub>3</sub> + H<sub>2</sub>O + 2Cl<sub>2</sub> → CaCl<sub>2</sub>+ CO<sub>2</sub> + 2HOCl
 Commercially, it is prepared by passing CO<sub>2</sub> into a suspension of bleaching powder, CaOCl<sub>2</sub> in water and then distilling:

$$2CaOCl_2 + CO_2 + H_2O \longrightarrow CaCl_2 + CaCO_4 + 2HOCl$$

## Structure:



#### **Properties:**

- 1. Strong or concentrated solution of HOCl is yellow in colour (because of dissolved Cl<sub>2</sub>) while dilute solution is colourless.
- 2. Highly unstable and decomposes into HCl and  $O_2$ . 2HOCl  $\longrightarrow$  2HCl +  $O_2$

3. Reacts with Mg to liberate 
$$H_2$$
.  
 $2HOCl + Mg \longrightarrow Mg(OCl)_2 + H_2$ 

- **4.** On distillation, decomposes to give  $H_2O$  and  $Cl_2O$ .  $2HOCl \longrightarrow Cl_2O + H_2O$
- 5. Acts as powerful oxidising and bleaching agent

$$\begin{aligned} & \text{HOCl} \longrightarrow \text{HCl} + \text{O} \\ \text{or } & \text{ClO}^{\ominus} + 2\text{H}^{\oplus} + 2e^{\ominus} \longrightarrow \text{Cl}^{\ominus} + \text{H}_2\text{O} \end{aligned}$$

**6.** In alkaline solution, oxidises chromic hydroxide to chromate.

$$2Cr(OH)_3 + 2NaClO + 4NaOH \longrightarrow 2Na_2CrO_4 +$$
 $3NaCl + 5H_2O$ 

## 4.16.2.2 Chlorous Acid, HClO<sub>2</sub>

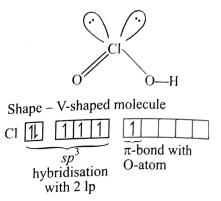
## Preparation:

Free chlorous acid (halous acids) have not been isolated (a)

An aq. solution of  $HClO_2$  is obtained by treating  $Ba(ClO_2)$  with dil.  $H_2SO_4$ .

$$Ba(ClO_2)_2 + H_2SO_4 \longrightarrow 2HClO_2 + BaSO_4 \downarrow$$

#### Structure:



#### **Properties:**

 Chlorous acid liberates iodine from iodides and thus acts as an oxidising agent.

$$4KI + NaClO_2 + 2H_2O \longrightarrow 4KOH + NaCl + 2I_2$$

2. It undergoes autooxidation at ordinary temperature and change into a mixture of HOCl and HClO<sub>3</sub>.

$$(+3)$$
  $(+1)$   $(+5)$   
2HClO<sub>2</sub>  $\longrightarrow$  HOCl + HClO<sub>3</sub>

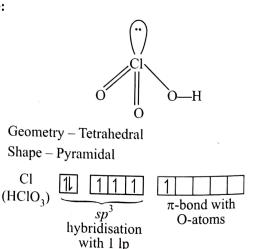
- 3. Possess bleaching property.
- 4. Freshly prepared solution is colourless, but it soon decomposes to ClO<sub>2</sub>, which colour the solution yellow.

## 4.16.2.3 Chloric Acid, HClO<sub>3</sub>

**Preparation:** By the action of dil.  $H_2SO_4$  on barium chlorate  $Ba(ClO_3)_2 + H_2SO_4 \longrightarrow BaSO_4 + 2HClO_3$ 

BaSO<sub>4</sub> is filtered off and unused BaSO<sub>4</sub> is precipitated by Baryta water, filterate is evaporated on vacuum dessicator over conc. BaSO<sub>4</sub>, until 40% solution of HClO<sub>3</sub> is obtained.

## Structure:



#### **Properties:**

1. Conc. HNO<sub>3</sub> is colourless, pungent smelling liquid fairly stable in dark. But undergoes decomposition on exposure to light.

## $_{3\text{HClO}_3} \xrightarrow{\Delta} \text{HClO}_4 + \text{Cl}_2 + \text{H}_2\text{O} + 2\text{O}_2$

2. On evaporation or distillation, HClO<sub>3</sub> undergoes disproportionation to give HClO<sub>4</sub>, the most stable oxyacid of Cl<sub>2</sub>.

$${}_{3\text{HClO}_2} \longrightarrow {}_{1\text{HClO}_4} + {}_{1\text{H}_2\text{O}} + {}_{2\text{ClO}_2}$$

- 3. Organic substances, e.g. paper, cotton, wool catch fire in contact with acid.
- 4. Acts as powerful oxidising and bleaching agent. On heating,

$$_{3\text{HClO}_{3}} \longrightarrow \text{HClO}_{4} + 2\text{ClO}_{2} + 2\text{H}_{2}\text{O}$$
 $_{2\text{ClO}_{2}} \longrightarrow \text{Cl}_{2} + 2\text{O}_{2}$ 

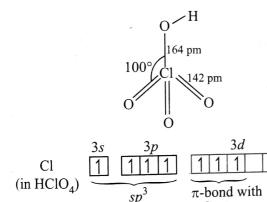
$$\begin{array}{ccc}
(+5) & (+7) & (0) \\
3HClO_3 & \longrightarrow HClO_4 + Cl_2 + 2O_2 + H_2O
\end{array}$$

## 4.16.2.4 Perchloric Acid, HCIO

## Preparation:

- 1. Anhydrous perchloric acid may be obtained by distilling a mixture of KClO<sub>4</sub> and conc. H<sub>2</sub>SO<sub>4</sub> under reduced pressure.  $KClO_4 + H_2SO_4 \longrightarrow KHSO_4 + HClO_4$ 
  - The distillate is yellow in colour owing to the presence of ClO, and HCl as impurities which are removed by blowing air through it.
- 2. By treating  $Ba(ClO_4)_2$  with dil.  $H_2SO_4$  and removing the insoluble BaSO<sub>4</sub> by filteration.

$$Ba(ClO_4)_2 + H_2SO_4 \longrightarrow 2HClO_4 + BaSO_4 \downarrow$$



hybridisation

### **Properties:**

- 1. Colourless, hygroscopic oily liquid (boiling point 292 K) which fumes in moist air.
- 2. It is unstable and decomposes on standing for few days even in dark, on heating, it decomposes with explosion.
- 3. It produces severe wound on the skin. On dehydration with  $P_4O_{10}$ , yields  $Cl_2O_7$ .  $4\mathrm{HClO_4} + \mathrm{P_4O_{10}} \longrightarrow 2\mathrm{Cl_2O_7} + 4\mathrm{HPO_3}$

## ILLUSTRATION 4.5

## Explain the following:

- a. More metal fluorides are ionic in nature than metal chlorides.
- b. Perchloric acid is a stronger acid than sulphuric acid.
- c. Fluorine does not undergo disproportionation reactions but other halogens do.

- a. According to Fajan's rules, a bigger anion is more easily polarised than a smaller anion by the same metal cation.  $F^{\Theta}$  ion is smaller in size in comparison to  $Cl^{\Theta}$  ion. Thus, the metal fluoride is more ionic than the metal chloride for the same metal cation.
- **b.** The oxidation state of chlorine in  $HClO_4$  is +7 while that of S in  $H_2SO_4$  is +6. This O—H bond in  $HClO_4$  is easily broken than in H<sub>2</sub>SO<sub>4</sub>. Hence, HClO<sub>4</sub> is a stronger acid in comparison to H<sub>2</sub>SO<sub>4</sub>.
- c. F being the most electronegative element shows only -1 oxidation/state while other halogens show both negative (-1) and positive (+1, +3, +5, +7) oxidation states. Thus, fluorine does not show disproportionation reactions but other halogens do.

## ILLUSTRATION 4.6

- a. Fluorine does not form oxyacid, but other halogens do. Why?
- **b.** Both NO and ClO<sub>2</sub> are odd electron species. NO dimerises but ClO<sub>2</sub> does not. Why?

- a. In oxy-acids, the central element always exhibits positive oxidation states. Fluorine, being the most electronegative, never shows positive oxidation states, hence F does not form oxy-acids. Other halogens have the tendency to show positive oxidation states and hence form oxy-acids.
- b. In NO, the size of nitrogen atom is small and the odd electron is attracted by only one oxygen atom while in ClO<sub>2</sub>, the size of chlorine atom is comparatively large and an odd electron is attracted by two oxygen atoms. As a result, the odd electron on N in NO is localised while the odd electron on chlorine in ClO2 is delocalised. Thus, NO has a tendency to dimerise but ClO2 does not.

## ILLUSTRATION 4.7

- a. Fluorine cannot be prepared from fluorides by chemical oxidation. Why?
- b. Anhydrous HCl is bad conductor of electricity while aqueous HCl is a good conductor. Give reason.
- Fresh iodine stain can be removed by washing with hypo solution. Explain.

#### Sol.

- a. The standard reduction potential of fluorine is maximum. Thus, it cannot be oxidised by any other reagent. Fluoride ion is very stable due to small size and high electronegativity of fluorine atom. Thus fluorine cannot be prepared from fluorides by chemical oxidation.
- b. In anhydrous state, HCl is a covalent molecule, hence bad conductor of electricity. Whereas, in aqueous state, HCl ionises and acts as good conductor.

$$HCl + H_2O \longrightarrow H_3O^{\oplus} + Cl^{\Theta}$$

c. Hypo solution, i.e. sodium thiosulphate, Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>.5H<sub>2</sub>O reacts with iodine to form water soluble colourless sodium tetrathionate and sodium iodide.

or 
$$2S_2O_3 + I_2 \longrightarrow 2NaI + Na_2S_4O_6$$

$$2S_2O_3^{2-} \longrightarrow S_4O_6^{2-} + 2e^{\Theta}$$

$$I_2 + 2e^{\Theta} \longrightarrow 2I^{\Theta}$$

$$2S_2O_3^{2-} + I_2 \longrightarrow S_4O_6^{2-} + 2I^{\Theta}$$

## 4.17 INTERHALOGEN COMPOUNDS

 $(AX_n, where X = 1, 3, 5 or 7)$ 

Due to difference in electronegativity, the halogen atoms combine with each other and gives rise to formation of binary covalent compounds called interhalogen compounds. In terms of composition, an interhalogen compound has one of the following stoichiometry.

	Oxidation state of A	Cl	Br	1
AX	+1	ClF	BrF, BrCl	(IF), ICl, IBr
$AX_3$	+3	ClF <sub>3</sub>	BrF <sub>3</sub>	IF <sub>3</sub> , I <sub>2</sub> Cl <sub>6</sub>
$AX_5$	+5	ClF <sub>5</sub>	BrF <sub>5</sub>	IF <sub>5</sub>
$AX_7$	+7	-	-	IF <sub>7</sub>

**Note:** In solid state 
$$I_2CI_6$$
 exists as:  $[ICI_2]^{\oplus}$   $[ICI_4]^{\ominus}$   $sp^3$   $sp^3d^2$  (<109°, 28') (90°)

A central atom is larger than B, i.e., A has less electronegativity than B. Interhalogen compounds are named as halides of less electronegative atom e.g. CIF is chlorine monofluoride rather than fluorine monochloride.

 $AX_n$ : Number of substituents A depends on the size of A as well as that of X. Thus, the bigger the size of A, the larger the number of X atoms it can carry, while the smaller the size of X, more of these can be accommodated around a given A atom.

#### Preparation:

1. By direct combination of the elements: However, the product formed by direct interaction of elemental halogens depends upon the conditions under which the reaction is carried out.

2. From lower interhalogens: By reacting lower interhalogens with halogens. This method is particularly used for the preparation of halogen fluorides, e.g.

$$\begin{aligned} \text{CIF} + \text{F}_2 &\longrightarrow \text{CIF}_3 & \text{CIF}_3 + \text{F}_2 &\xrightarrow{350^{\circ}\text{C}} \text{CIF}_5 \\ & \text{(Excess)} \end{aligned}$$

$$\text{BrF}_3 + \text{F}_2 \xrightarrow{200^{\circ}\text{C}} \text{BrF}_5 & \text{IF}_5 + \text{F}_2 \xrightarrow{270^{\circ}\text{C}} \text{IF}_7 \end{aligned}$$

3. Miscellaneous methods:

6HCl+ KIO<sub>3</sub> + 2KI → 3KCl + 3H<sub>2</sub>O + 3ICl  
Cl<sub>2</sub> + ClF<sub>3</sub> 
$$\xrightarrow{200^{\circ}-600^{\circ}C}$$
 3ClF  
KCl+ 3F<sub>2</sub>  $\xrightarrow{200^{\circ}C}$  KF + ClF<sub>5</sub>  
3I<sub>2</sub> + 5AgF → 5AgI + IF<sub>5</sub>

#### **Properties:**

- 1. Physical state: Interhalogen compounds may be covalent Physical State. Bry CIF<sub>3</sub>, IF<sub>7</sub>), liquids (BrF<sub>3</sub>, BrF<sub>5</sub>, IF<sub>5</sub>) or  $_{SO[id_8]}$  gases (CIF, BrF, CIF<sub>3</sub>, IF<sub>7</sub>), liquids (BrF<sub>3</sub>, BrF<sub>5</sub>, IF<sub>5</sub>) or  $_{SO[id_8]}$ (ICl, IBr, IF<sub>3</sub>, ICl<sub>3</sub>).
- 2. Colour: Although many interhalogen compounds of F colourless those having heavier halogens are coloured The colour becomes deeper with an increase in atomic weight of the compound.
- 3. Diamagnetic nature: Since all the valence electrons are present as bonding or non-bonding (lone pairs) electron pairs, these compounds are diamagnetic in nature.
- 4. Heat of formation: It is of low magnitude. These are extremely volatile compounds. In general compounds containing fluorine are more volatile than those containing Cl, Br or I.
- 5. Boiling point: For each type of interhalogen compound the boiling point increases with increase in electronegativity difference between A and X.
- 6. Thermal stability: For AX type, thermal stability decreases with decrease in electronegativity difference between A and X. IF (1.5) > BrF (1.2) > ClF (1.0) > ICl (0.5) > IBr (0.3)BrCl (0.2).

The greater the electronegativity difference, more polar is the A-X bond and hence greater the thermal stability.

- 7. Reactivity: In general interhalogen compounds are more reactive than halogens (except F<sub>2</sub>). This is because (X—X) bond in interhalogens is weaker than (X-X) bond in halogens except F-F bond.
- 8. Hydrolysis: All these undergo hydrolysis giving halide ion derived from the smaller halogen and a hypohalite (when XX'), halite (when  $XX'_3$ ), halate (when  $XX'_5$ ) and perhalate (when XX'<sub>7</sub>) anion derived from larger halogen:

(i) 
$$XX' + H_2O \longrightarrow HX' + HOX$$

(ii) 
$$XX'_3 + 2H_2O \longrightarrow HX' + HXO_2$$

$$(iii)XX'_5 + 3H_2O \longrightarrow HX' + HXO_3$$

$$(iv)XX'_7 + 4H_2O \longrightarrow HX' + HXO_4$$

$$XX'$$
 $XX'_3$ 
 $XX'_5$ 
 $XX'_7$ 
 $(e.g., BrCl, ICl)$ 
 $(e.g., ICl_3)$ 
 $(e.g., IF_5, BrF_5, (e.g., IF_7)$ 
 $ClF_5)$ 

(i) 
$$XX'$$
: BrCl + H<sub>2</sub>O  $\longrightarrow$  HCl + HOBr

Hypobromous acid

(ii) 
$$XX'_3$$
:  $ICl_3 + 2H_2O \longrightarrow 3HCl + HIO_2$ 

Iodous acid

(iii) 
$$XX'_5$$
:  $IF_5 + 3H_2O \longrightarrow 5HF + HIO_3$ 

(iv) 
$$XX'_7$$
: IF<sub>7</sub> + 4H<sub>2</sub>O  $\longrightarrow$  7HF + HIO<sub>4</sub>

Periodic acid

Interhalogen compounds reacts with  $F^{\Theta}$  accepter to form cationic species.

$$\begin{array}{c} \operatorname{ClF}_3 + \operatorname{BF}_3 \longrightarrow [\operatorname{ClF}_2]^{\oplus} [\operatorname{BF}_4]^{\ominus} \\ \operatorname{ClF}_3 + \operatorname{SbF}_5 \longrightarrow [\operatorname{ClF}_2]^{\oplus} [\operatorname{SbF}_6]^{\ominus} \\ \operatorname{ClF}_3 + \operatorname{PtF}_5 \longrightarrow [\operatorname{ClF}_2]^{\oplus} [\operatorname{PtF}_6]^{\ominus} \end{array}$$

9. Interhalogens also form addition compounds with alkali halides. These compounds are ionic, and are called polyhalides.

$$\begin{split} & \text{ICl} + \text{NaBr} \longrightarrow \text{Na}^{\oplus} \left[ \text{BrICl} \right]^{\ominus} \\ & \text{ICl} + \text{KI} \longrightarrow \text{K}^{\oplus} \left[ \text{I}_2 \text{Cl} \right]^{\ominus} \\ & \text{BrF}_5 + \text{CsF} \longrightarrow \text{Cs}^{\oplus} \left[ \text{BrF}_6 \right]^{\ominus} \\ & \text{IF}_5 + \text{KI} \longrightarrow \text{K}^{\oplus} \left[ \text{IF}_6 \right]^{\ominus} \\ & \text{ICl}_3 + \text{KCl} \longrightarrow \text{K}^{\oplus} \left[ \text{ICl}_4 \right]^{\ominus} \end{split}$$

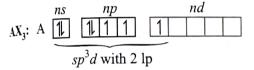
10. As non-aqueous ionising solvents:

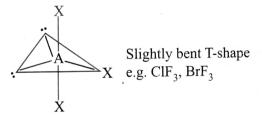
$$2BrF_3 \rightleftharpoons [BrF_2]^{\oplus} + [BrF_4]^{\ominus}$$

Thus substances producing  $[BrF_2]^{\oplus}$  ions are acids and  $[BrF_4]^{\ominus}$  ions are bases in  $BrF_3$  (solvent).

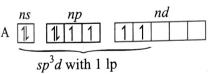
## Structure and shapes on the basis of VBT:

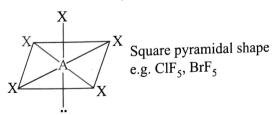
AX: A 
$$ns$$
  $np$  e.g., ICl  $i$  I—Cl  $sp^3$  hybridised with 3 lp linear shape



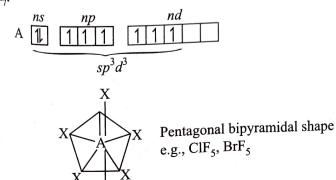


AX<sub>5</sub>:





AX<sub>7</sub>:



e.g., IF<sub>7</sub> (It is probably the only known example of a non-transition element using three *d*-orbitals for bonding.)

## Structure and shapes on the basis of VSEPR theory:

Mole- cule	Total number of electron	Bond pairs	Lone	Geometry (shape)
cuie	pairs on A	pairs	pans	
AX	$\frac{7+(1\times 1)}{2}=4$	1	3	Tetrahedral (Linear)
	ν ε΄τ , <b>ν</b>			X
AX <sub>3</sub>	$\frac{7+(1\times3)}{2}=5$	3	2	Bent T-shape
				:AX
		3 V ( )		X
AX <sub>5</sub>	$\frac{7+(1\times 5)}{2}=6$	5	1	Octahedral (square pyramidal)
				X
				X
AX <sub>7</sub>	$\frac{7 + (1 \times 6)}{2} = 7$	7	0	Pentagonal bipyramidal
				$X \xrightarrow{X} X$

## 4.18 POLYHALIDE IONS

Ions like  $I_3^{\ominus}$ ,  $IBr_2^{\ominus}$ ,  $IBrF^{\ominus}$ ,  $CIF_4^{\ominus}$ , etc. which contain more than two, same or different halogen atoms are called polyhalide ions and the corresponding compound is called **polyhalide**.

**Preparation:** Alkali metal halides either in solution or in crystalline salts react with halogens or interhalogen compounds forming ionic polyhalide compounds.

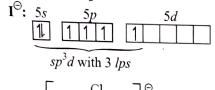
$$\begin{aligned} & \text{KI} + \text{I}_2 \longrightarrow \text{KI}_3 \\ & \text{KBr} + \text{ICl} \longrightarrow \text{KIBrCl} \\ & \text{KF} + \text{BrF}_3 \longrightarrow \text{KBrF}_4 \\ & \text{F}^{\circleddash} + \text{ClF}_3 \longrightarrow \text{ClF}_4^{\circleddash} \end{aligned}$$

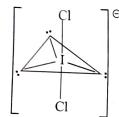
A list of the principle types of polyhalide species which have been characterised are as follows:

Number of halogen atoms in the anion			
3	5	7	9
$Br_3^{\Theta}$ , $ClF_2^{\Theta}$ , $IBrF^{\Theta}$	ClF <sub>4</sub> <sup>⊙</sup> , ICl <sub>3</sub> F <sup>⊙</sup>	$\operatorname{BrF}_{6}^{\Theta}, \operatorname{I}_{7}^{\Theta}$	I°⊝
$I_3^{\odot}$ , $IBr_2^{\widetilde{\odot}}$ , $IBrCl^{\odot}$	BrF₄ <sup>⊖</sup>	IF <sub>6</sub> <sup>⊖</sup> , BrF <sub>6</sub> <sup>⊝</sup>	BrF <sub>5</sub>
ICl₂ <sup>⊖</sup>	IF <sub>4</sub> <sup>⊖</sup>	ClBr <sub>6</sub> <sup>⊙</sup>	
BrCl <sub>2</sub> <sup>⊖</sup>	ICl₄ <sup>⊖</sup>		
BrI <sub>2</sub> ⊖			
$ClBr_2^{\Theta}$	-		

Shape of polyhalide ions: Trihalides or polyhalides containing three atoms

$$ICl_2^{\Theta}, I_3^{\Theta}, IBr_2^{\Theta}$$



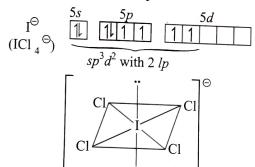


Linear: Bond angle is of the order of 171-179°

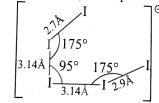
Surprisingly,  ${\rm I_3}^{\ominus}$  and  ${\rm Br_3}^{\ominus}$  are slightly unsymmetrical i.e. the two I—I bonds are not equal lengths.

Polyhalides containing five atoms

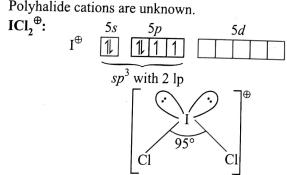
 ${\rm ICl_4}^{\circleddash}$ ,  ${\rm BrF_4}^{\circleddash}$  are square planar.

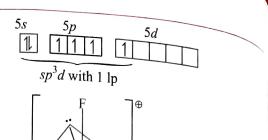


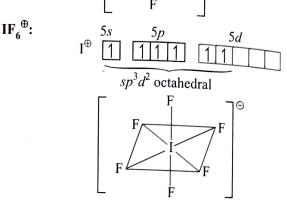
 ${\rm I_5}^{\circleddash}$  in  ${\rm NMe_4I_5}$  is approximately L-shaped.



Polyhalide cations are unknown.







#### **Properties:**

IF₄<sup>⊕</sup>:

1. They are unstable towards thermal dissociation into monohalides and halogen or interhalogen compound. The lighter halogen atom remains with the metal atom.

**a.** 
$$CsICl_2 \xrightarrow{\Delta} CsCl + I^{\ominus}Cl$$
  $ICl_2 \xrightarrow{\ominus} \xrightarrow{\Delta} Cl^{\ominus} + I^{\ominus}Cl$   
**b.**  $CsICl_2 \xrightarrow{} CsI + Cl_2$   $ICl_2 \xrightarrow{\ominus} \xrightarrow{} I^{\ominus} + Cl_2$ 

Path (a) is favoured energetically by the high lattice energy of CsCl, i.e., metal halide formed is the one with high lattice energy.

2. Thermal stability of a given type of polyhalide anion increases with the increasing size of the cation.

$$NaI_3^{\ominus} > KI_3^{\ominus}$$

For trihalides formed by same metal, order of thermal stability based on dissociation pressure is

$$I_3^{\ominus} > IBr_2^{\ominus} > ICl_2^{\ominus} > I_2Br^{\ominus} > Br_3^{\ominus} > BrCl_2^{\ominus} > Br_2Cl^{\ominus}$$

Thermal stability is enhanced, the more symmetrical the polyhalide ion and larger the size of central atom and hence the order.

3. Reaction with halogens: The metal polyhalides can often be converted into compounds containing other polyhalides by the action of halogens.

$$\begin{array}{c} \operatorname{IBr}_{2}^{\ominus} + \operatorname{Cl}_{2} \longrightarrow \operatorname{ICl}_{2}^{\ominus} + \operatorname{Br}_{2} \\ \operatorname{IBrCl}^{\ominus} + \operatorname{ICl} \longrightarrow \operatorname{ICl}_{2}^{\ominus} + \operatorname{IBr} \\ \operatorname{ICl}_{2}^{\ominus} + \operatorname{Cl}_{2} \longrightarrow \operatorname{ICl}_{4}^{\ominus} \end{array}$$

4. Dissociation in aqueous solution: The metal polyhalides are unstable in water, leading to a mixture of products which appears to arise from hydrolysis of the interhalogen compound released.

 $5ICl_4^{\Theta} + 9H_2O \implies I_2 + 3IO_3^{\Theta} + 20Cl^{\Theta} + 18H^{\theta}$ ICl<sub>4</sub> dissociates in aq. solution to metal chloride and ICl<sub>y</sub>

then hydrolyse to 
$$ICl_3^{\ominus}$$
 and  $I_2$ .

$$ICl_4^{\ominus} \longrightarrow Cl^{\ominus} + ICl_3$$

$$5ICl_3 + 9H_2O \longrightarrow 3IO_3^{\ominus} + 15Cl^{\ominus} + I_2$$

5. polyhalides dissolve in non-aqueous media, act as halogenating agents, e.g. polybromides have been used in the bromination of β-naphthal, aniline etc.

# 4.19 PSEUDOHALIDES AND PSEUDOHALOGENS

A few ions are known, consisting of two or more electronegative aforms of which at least one is nitrogen, that have properties similar of those of halide ions. These ions are called pseudohalide ions. These ions are called pseudohalide ions are univalent and these form salts resembling pseudohalide salts. For example, sodium salts are soluble in water but the silver salts are insoluble. The hydrogen compounds are acids like the halogen acids, HX. The pseudohalide ions are:

like the hard  $(CN^{\Theta})$ ; Isocyanide ion  $(NC^{\Theta})$  Isocyanate ion  $(NC^{\Theta})$  Isocyanate ion  $(NC^{\Theta})$  Isocyanate ion  $(NC^{\Theta})$  Isothiocyanate ion  $(NC^{\Theta})$  Isothiocyanate ion  $(NC^{\Theta})$  Isothiocyanate ion  $(NC^{\Theta})$  Tellurocyanate ion  $(NC^{\Theta})$  Azido carbon disulphide ion  $(NC^{\Theta})$  Azido carbon disulphide ion  $(NC^{\Theta})$ 

The salts formed by above ions are called pseudohalides. As the dimers of halide ions are called halogens, the covalent dimers of the pseudohalide ions are called pseudohalogens or halogenoids. So far only few of pseudohalogens have been isolated and characterised. The pseudohalogens known are:

Cyanogen (CN)<sub>2</sub>; Oxycyanogen (OCN)<sub>2</sub> Thiocyanogen (SCN)<sub>2</sub>; Selenocyanogen (SeCN)<sub>2</sub> Tellurocyanogen (TeCN)<sub>2</sub>; Azido carbon disulphide (SCSN<sub>3</sub>)<sub>2</sub>

The best known pseudohalide is  $CN^{\Theta}$ . This resembles  $Cl^{\Theta}$ ,  $Br^{\Theta}$  and  $I^{\Theta}$  in the following respects:

- i. It forms an acid, HCN.
- ii. It can be oxidised to (CN)2 molecule.
- iii. It forms insoluble salts with  $Ag^{\oplus}$ ,  $Pb^{2+}$  and  $Hg_2^{2+}$ .
- iv. It forms large number of complexes similar to halide complexes, e.g.,

$$[\text{Cu(CN)}_4]^{2-}$$
 and  $[\text{CuCl}_4]^{2-}$ ,  $[\text{Co(CN)}_6]^{3-}$  and  $[\text{CoCl}_6]^{3-}$ 

- Inter-pseudohalogen compounds CICN, BrCN and ICN can be formed.
- vi. AgCN is insoluble in water but soluble in ammonia like AgCl.
- vii. HCN is oxidised like HCl.

$$MnO_2 + 4HCN \longrightarrow Mn(CN)_2 + (CN)_2 + 2H_2O$$
  
 $MnO_2 + 4HCl \longrightarrow MnCl_2 + Cl_2 + 2H_2O$ 

### ILLUSTRATION 4.8

Which species of  $I_2Cl_6$  in solid state exist in  $sp^3$  and  $sp^3d^2$ -hybridised state?

Sol. In solid state I<sub>2</sub>Cl<sub>6</sub> exist as:

$$[ICl_{2}]^{\oplus} \qquad [ICl_{4}]^{\odot}$$

$$sp^{3} \qquad sp^{3}d^{2}$$

$$(<109^{\circ}, 28') \qquad (90^{\circ})$$

$$: [^{\oplus}Cl \qquad [2lp + 2bp] \Rightarrow sp^{3}$$
hybridised

$$\begin{array}{c|c} Cl \\ \ominus \\ Cl \\ Cl \end{array} \quad [2lp + 4bp] \Rightarrow sp^3d^2 \\ Cl \\ Cl \\ hybridised \end{array}$$

# 4.20 BLEACHING POWDER,

CaOCl<sub>2</sub>·H<sub>2</sub>O

Bleaching powder is also called calcium chlorohypochlorite because it is considered as a mixed salt of hydrochloric acid and hypochlorous acid.

It is manufactured by the action of chlorine on dry slaked lime, Ca(OH)<sub>2</sub>, at 40°C.

$$Ca(OH)_2 + Cl_2 \longrightarrow Ca(OC1)C1 + H_2O$$

### **Properties:**

a. It is a pale yellow powder. It has a strong smell of chlorine. It is soluble in water but a clear solution is never formed due to the presence of impurities.

On account of the formation of nascent oxygen, it shows oxidising and bleaching properties.

b. Oxidising properties:

$$\begin{aligned} \text{CaOCl}_2 + \text{H}_2\text{S} &\longrightarrow \text{CaCl}_2 + \text{H}_2\text{O} + \text{S} \\ \text{CaOCl}_2 + 2\text{FeSO}_4 + \text{H}_2\text{SO}_4 &\longrightarrow \text{Fe}_2(\text{SO}_4)_3 + \text{CaCl}_2 + \text{H}_2\text{O} \\ \text{CaOCl}_2 + \text{KNO}_2 &\longrightarrow \text{CaCl}_2 + \text{KNO}_3 \\ 3\text{CaOCl}_2 + 2\text{NH}_3 &\longrightarrow 3\text{CaCl}_2 + 3\text{H}_2\text{O} + \text{N}_2 \\ \text{CaOCl}_2 + 2\text{KI} + 2\text{HCl} &\longrightarrow \text{CaCl}_2 + 2\text{KCl} + \text{H}_2\text{O} + \text{I}_2 \\ \text{Na}_3\text{AsO}_3 + \text{CaOCl}_2 &\longrightarrow \text{CaCl}_1 + \text{Na}_3\text{AsO}_4 \end{aligned}$$

c. Bleaching action:

Coloured matter  $+ [O] \longrightarrow Colourless product$ 

**d.** It loses its chlorine by the action of dilute acids (in excess) or carbon dioxide.

$$\begin{aligned} &\text{CaOCl}_2 + 2\text{HCl} \longrightarrow \text{CaCl}_2 + \text{H}_2\text{O} + \text{Cl}_2 \\ &\text{CaOCl}_2 + \text{H}_2\text{SO}_4 \longrightarrow \text{CaSO}_4 + \text{H}_2\text{O} + \text{Cl}_2 \\ &\text{CaOCl}_2 + \text{H}_2\text{SO}_4 \longrightarrow \text{CaSO}_3 + \text{H}_2\text{O} + \text{Cl}_2 \end{aligned}$$

The amount of chlorine obtained from a sample of bleaching powder by treatment with excess of dilute acids or carbon dioxide is called available chlorine. A good sample of bleaching powder contains 35–38% of available chlorine.

Uses: It is used (i) as a disinfectant and germicide especially in the sterilisation of drinking water, (ii) for manufacture of chloroform, (iii) for making wool unshrinkable, (iv) as an oxidising agent in industry and (v) mainly as bleaching agent for cotton, linen and wood pulp. However, delicate articles like straw, silk, ivory, etc., are not bleached by bleaching powder.

Estimation of available chlorine: The maximum percentage of available chlorine as calculated from **Odling's formula** comes to 49%.

$$CaOCl_2 \cdot H_2O + H_2SO_4 \longrightarrow CaSO_4 + 2H_2O + Cl_2$$
  
M. mass = 145

145 g of bleaching powder contains 71 g chlorine 100 g of bleaching powder contains  $71/145 \times 100 = 49$  g chlorine The estimation of available chlorine in a given sample of bleaching powder is done volumetrically by the following method.

**lodometric method:** A weighed quantity of bleaching powder is suspended in water and treated with excess of acetic acid and potassium iodide. The liberated iodine is estimated by treating with a standard solution of sodium thiosulphate using starch as an indicator.

$$CaOC1_2 + 2CH_3COOH \longrightarrow (CH_3COO)_2Ca + Cl_2 + H_2O$$

$$2Kl + Cl_2 \longrightarrow 2KCl + I_2$$

$$2Na_2S_2O_3 + I_2 \longrightarrow 2Nal + Na_2S_4O_6$$

Let  $V \text{ mL of } N/x \text{ Na}_2 \text{S}_2 \text{O}_3$  be used for W g of a sample of bleaching powder.

 $V \text{ mL of } N/x \text{ Na}_2S_2O_3 \text{ and } V \text{ mL of } N/x \text{ Iodine}$ 

= 
$$V \text{ mL } N/x \text{ Chlorine} = \frac{35.5}{x} \times \frac{V}{1000} \text{ g Chlorine}$$

Thus, % of available chlorine

$$=\frac{35.5\times V\times 100}{x\times 1000\times W}=\frac{35.5\times V}{x\times W}$$

The percentage of available chlorine in the commercial samples of bleaching powder is usually between 33% and 38%. The low value is due to the following factors:

- Incomplete reaction between slaked lime and chlorine during its formation.
- **ii.** Impurities present in the original slaked lime used for the manufacture.
- iii. Decomposition of bleaching powder when kept in air.

### ILLUSTRATION 4.9

Explain the following:

- a. Dry chlorine does not bleach clothes.
- **b.** Fluorine does not form  $F_3^{\ominus}$  (polyhalide) ion.
- c. HF is least volatile and HCl is most volatile amongst hydrogen halides.

### Sol.

a. Chlorine acts as a bleaching agent only in the presence of moisture or water, due to liberation of nascent oxygen from water

$$Cl_2 + H_2O \longrightarrow 2HCl + [O]$$

Hence dry chlorine cannot bleach clothes.

- **b.** Fluorine due to absence of *d*-orbitals in its valence shell cannot expand its coordination number beyond one. Hence  $F_3^{\Theta}$  ion is not known.
- c. In covalent compounds, the boiling point increases with increase of molecular mass, as van der Waals forces increases. The volatility, thus decreases in covalent compounds with increase in molecular mass. However, hydrogen bonding is present in HF. Due to which, the boiling point of HF is higher and the volatility is less. Thus the volatility of hydrogen halides can be represented as

Volatility: HCl > HBr > HI > HF

### ILLUSTRATION 4.10

- a. Pure HI kept in a bottle acquires a brown colour after sometime. Why?
- b. Ferric iodide is very unstable but ferric chloride is stable.
  Why?
- c. KHF<sub>2</sub> is well known but KHCl<sub>2</sub> and KHBr<sub>2</sub> do not exist. Why?

### Sol.

a. HI is a strong reducing agent. It is oxidised by oxygen of the air, i.e. aerial oxidation of HI occurs.

$$O_{2} + 4H^{\oplus} + 4e^{\Theta} \longrightarrow 2H_{2}O$$

$$[2I^{\Theta} \longrightarrow I_{2} + 2e^{\Theta}] \times 2$$

$$O_{2} + 4H^{\oplus} + 4I \longrightarrow 2H_{2}O + 2I_{2}$$

The iodine liberated gives a brown colour to the solution

- b. Iodide ion is a strong reducing agent and reduces ferric ions into ferrous ions, hence ferric iodide is unstable. On the other hand, chloride ion is a weak reducing agent and does not reduce ferric to ferrous ion and thus ferric chloride is stable.
- c. Hydrofluoric acid exists as dimeric molecule  $(H_2F_2)$  due to hydrogen bonding. HF thus exhibits dibasic nature and forms two series of salts, KHF $_2$  (as K $^\oplus$  and F $^\ominus$  ..... H–F) and KF (K $^\oplus$  and F $^\ominus$ ). HCl and HBr exist as monomeric molecules as hydrogen bonding is not present.

### ILLUSTRATION 4.11

- a. Iodine dissolves more in KI solution than in water. Why?
- b. Colour of KI solution containing starch turns deep blue when chlorine water is added. Explain.

### Sol.

a. Iodine,  $I_2$  is a covalent molecule. Hence it is less soluble in polar solvent, i.e. water,  $H_2O$ . In KI solution, KI reacts with water to form  $KI_3$  which is an ionic compound  $K^{\oplus} I_3^{\ominus}$ . Being ionic,  $KI_3$  is more soluble in water.

$$KI + I_2 \Longrightarrow K^{\oplus} I_3^{\ominus}$$

b. Chlorine being a strong oxidising agent displaces iodine from KI i.e., oxidises  $I^{\Theta}$  to  $I_2$ . Iodine is absorbed by starch and thus deep blue coloured solution is obtained due  $\mathbb{N}$  formation formed of starch  $-I_2$  adsorption complex.

$$2KI + Cl_2 \longrightarrow 2KCl + I_2$$

 $I_2 + Starch \longrightarrow [Starch - I_2]$  adsorption complex

### ILLUSTRATION 4.12

Mention the conditions in which the following statements are correct.

- a. Chlorine is a good bleaching agent.
- **b.** A mixture of H<sub>2</sub> and Cl<sub>2</sub> explodes.
- c. Cl<sub>2</sub> reacts with NaOH solution to produce sodium chloride and sodium hypochlorite (along with water).
- d. Cl<sub>2</sub> reacts with NaOH solution to produce sodium chloride and sodium chlorate (along with water).
- e. Cl<sub>2</sub> substitutes hydrogen atoms of a molecule of methane.
- f. Cl<sub>2</sub> reacts with ammonia to form nitrogen and ammonium chloride.
- g. Cl<sub>2</sub> reacts with lime to form bleaching powder.
- h. Iodine dissolves freely in water.
- Chlorine forms an addition product with SO<sub>2</sub>.

- In presence of moisture, chlorine acts as a good bleaching
- b. A mixture of H<sub>2</sub> and Cl<sub>2</sub> explodes on exposure to direct
- Cl, reacts with NaOH solution to produce NaCl, sodium hypochlorite and H<sub>2</sub>O in cold and dilute conditions.
- When NaOH solution is hot and concentrated, it reacts with Cl. to produce sodium chloride, sodium chlorate and water.
- e in diffused sunlight, Cl<sub>2</sub> substitutes hydrogen atoms of a molecule of methane.
- f. When NH3 is in excess, it reacts with Cl2 to form N2 and
- g. On passing Cl<sub>2</sub> over dry slaked lime, bleaching powder is
- h. lodine dissolves freely in water in presence of KI.
- i, ln dry conditions, Cl<sub>2</sub> forms an addition product with SO<sub>2</sub>.

### CONCEPT APPLICATION EXERCISE 4.1

- 1. Bond dissociation energy of F<sub>2</sub> is less than that of Cl<sub>2</sub>. Give reason.
- 2. Why fluorine does not exhibit any positive oxidation state?
- Bleaching of flowers by chlorine is permanent, while that by sulphur dioxide is temporary. Explain.
- 4. Arrange HOCl, HClO2, HClO3 and HClO4 in order of (i) acidic strength and (ii) oxidising power. Give reason.
- 5. The negative value of electron gain enthalpy is less for fluorine than for chlorine. Why?
- 6. Despite the fact than fluorine is more electronegative than iodine, yet HF is less acidic as compared to HI. Explain.
- 7. What happens when Cl<sub>2</sub> is passed through a hot concentrated solution of a base like Ba(OH)<sub>2</sub>?
- 8. Why fluorine never acts as the central atom in polyatomic interhalogen compounds?
- 9. ClF<sub>3</sub> exists but FCl<sub>3</sub> does not. Why?
- 10. Addition of Cl<sub>2</sub> to KI solution gives it a brown colour but excess of Cl<sub>2</sub> turns it colourless. Why?
- 11. Give relevant chemical equations for the preparation of:
  - a. Chlorine from sodium chloride.
  - b. Iodine from Kelp.
  - c. Hydrobromic acid from potassium bromide.
  - d. Bleaching powder from slaked lime.
  - e. KClO<sub>2</sub> from sodium chloride.
- 12. A sodium salt (A) is heated with conc. sulphuric acid. The evolved gas turns moist litmus paper red and produces white fumes in contact with a glass rod moistened with ammonia solution. It also gives white precipitate when passed through AgNO3 solution. When the salt is heated with MnO<sub>2</sub> and conc. H<sub>2</sub>SO<sub>4</sub>, a gas with an irritating smell is evolved which turns starch-iodide paper blue. Identify the salt and the gaseous product evolved from it. Explain your answer with relevant chemical equations.

- 13. A certain compound (X) shows the following reactions.
  - When KI is added to an aqueous suspension of (X) containing acetic acid, iodine is liberated.
  - b. When CO2 is passed through an aqueous suspension of (X), the turbidity transforms to a precipitate.
  - c. When the paste of (X) in water is heated with ethyl alcohol, a product of anaesthetic use is obtained. Identify (X) and write down chemical equations for reactions at steps (a), (b) and (c).
- 14. A colourless inorganic compound (A) imparts a green colour to flame. Its solution does not give any precipitate with H2S. Its solution gives white precipitate with conc. H<sub>2</sub>SO<sub>4</sub> which is insoluble in dil. H<sub>2</sub>SO<sub>4</sub>. When it is heated with K2Cr2O7 and conc. H2SO4, a red gas is evolved. The gas when passed through aqueous NaOH solution turns it yellow. Identify the compound (A) and give chemical reactions.
- 15. Give balanced chemical reactions for the following:
  - i. Sodium iodate is treated with sodium bisulphite solution.
  - ii. Chlorine is passed through hot NaOH solution.
  - iii. Chlorine is passed through aqueous potassium hydroxide.
  - iv. Chlorine gas is bubbled through a solution of ferrous
  - v. Iodine reacts with conc. HNO<sub>3</sub>.
  - vi. Chlorine is passed over slaked lime.
  - vii. Sodium chloride is heated with K2Cr2O7 and conc. H<sub>2</sub>SO<sub>4</sub>.
  - viii. Potassium iodide is heated with MnO<sub>2</sub> conc. H<sub>2</sub>SO<sub>4</sub>.
  - ix. Chlorine reacts with Na<sub>2</sub>SO<sub>3</sub> solution.
  - x. Iodine is added to stannous chloride solution.
  - xi. Chlorine is passed through a suspension of iodine.
  - xii. Cl<sub>2</sub> is passed through a suspension of CaCO<sub>3</sub>.
  - xiii. Chlorine gas is passed through dry and aqueous sulphur dioxide.
  - xiv. Bromine reacts with Na<sub>2</sub>CO<sub>3</sub> solution.
  - xv. Potassium iodide is added to bleaching powder containing dilute acetic acid.
- 16. Pseudohalogens or halogenides are complex molecules which behaves like halogens. Among the following list CN<sup>©</sup> (cyanide), OCN<sup>©</sup> (cyanate), SCN<sup>©</sup> (thio-cyanate)  $SeCN^{\Theta}$  (selenocyanate),  $TeCN^{\Theta}$  (tellurocyanate)  $ONC^{\odot}$  (isocyanate),  $N_3^{\odot}$  (azide), cyanogen  $(CN)_2$ oxycyanogen  $(OCN)_2$ thiocyanogen (SCN)<sub>2</sub> tellurocyanogen (TeCN)2, azidecarbon disulphide (SCS N<sub>3</sub>), CICN, BrCN, ICN, ICI, IF<sub>7</sub>, IF<sub>5</sub>, I<sub>3</sub> $^{\odot}$ , ICI,  $^{\odot}$ ,  $I^{\Theta}, I^{\oplus}, I_{3}^{\oplus}$ .
  - a. Which are interpseudohalogens?
  - **b.** Which are interhalogens or their anions?
  - **c.** Which are polyhalides?
  - d. Which are neither (a), (b), (c) or pseudohalogen or their anions?
  - e. Which are pseudohalogens or their anions?

17. When carnalite is crystallised, the mother liquor contains a more water soluble salt (X) which gives pink mass in cobalt nitrate test when (X) is heated with conc. H<sub>2</sub>SO<sub>4</sub> brown gas is evolved. (X) gives, with AgNO<sub>3</sub> solution, a pale yellow (Cream. Coloured) ppt. slightly soluble in NH<sub>4</sub>OH. Identify (X).

# Solved Examples

### EXAMPLE 4.1

- a. What happens when Cl<sub>2</sub> reacts with cold dilute solution of sodium hydroxide?
- b. Why does chlorine water lose its yellow colour on standing?

### Sol.

a. With cold dilute solution of sodium hydroxide, Cl<sub>2</sub> undergoes disproportionation to give a mixture of sodium chloride, NaCl and sodium hypochlorite (NaOCl).

$$Cl_2 + 2NaOH \longrightarrow NaCl + NaOCl + H_2O$$

**b.** Chlorine water is yellow due to the presence of hypochlorous acid, HOCl. On standing, HOCl being unstable decomposes to form HCl. Hence the yellow colour disappears.

$$Cl_2 + H_2O \longrightarrow HCl + HOCl \longrightarrow 2HCl + [O]$$
yellow colourless

### EXAMPLE 4.2

- a. When a moist blue litmus paper is dipped in a solution of hypochlorous acid, it first turns red and then latter gets decolourised. Explain.
- b. Iodine is liberated when KI is added to a solution of Cu<sup>2+</sup> ions but Cl<sub>2</sub> is not liberated when KCl is added to a solution of Cu<sup>2+</sup> ions. Why?

### Sol

**a.** Hypochlorous acid, HOCl behaves as an acid and hence blue litmus paper turns red.

$$HOCl \longrightarrow H^{\oplus} + OCl^{\ominus}$$

Hypochlorous acid also acts as a bleaching agent and thus decolourises red litmus by the nascent oxygen.

$$HOCl \longrightarrow HCl + [O]$$

**b.** The iodide ion  $(I^{\Theta})$  being a strong reducing agent, reduces  $Cu^{2^+}$  to  $Cu^{\oplus}$  and itself gets oxidised to  $I_2$ .

$$2Cu^{2+} + 4KI \longrightarrow Cu_2I_2 + I_2 + 4K^{\oplus}$$

Since  $Cl^{\Theta}$  ion does not act as a reducing agent, therefore,  $Cl_2$  is not liberated when KCl is added to a solution of  $Cu^{2+}$  ions.

### EXAMPLE 4.3

 $Na_2S_2O_3$  reacts with  $Cl_2$  and  $l_2$  to give different oxidation products. Give the equations involved and a plausible explanation of their contrasting behaviour.

Sol.  $Cl_2$  is a stronger oxidising agent than  $I_2$  and hence oxidises  $Na_2S_2O_3$  to  $NaHSO_4$  in which the oxidation state of S increases

from +2 to +6, while with only  $I_2$  solution, sodium tetrathionally  $Na_2S_4O_6$  is obtained in which the oxidation state of S increases from +2 to +2.5 only.

(+2) (+6)  

$$Na_2S_2O_3 + 4CI_2 + 5H_2O \longrightarrow 2 \text{ NaHSO}_4 + 8HCI}$$
  
(+2) (+2.5)  
 $Na_2S_2O_3 + I_2 \longrightarrow Na_2S_4O_6 + 2NaI$ 

### EXAMPLE 4.4

A liquid 'A' is treated with Na<sub>2</sub>CO<sub>3</sub> solution. A mixture of two salts 'B' and 'C' is produced in the solution. The mixture on acidification with sulphuric acid and distillation produces the liquid 'A' again. Identify 'A', 'B' and 'C' and write the equations involved.

Sol. 
$$A + Na_2CO_3 \longrightarrow B + C \xrightarrow{N_2SO_4} A$$

Liquid 'A' is bromine, which on treatment with Na<sub>2</sub>CO<sub>3</sub> forms a mixture of NaBr and BaBrO<sub>3</sub>. The mixture on acidification and distillation gives liquid bromine again.

$$2Br_2 + 3Na_2CO_3 \longrightarrow 5NaBr + NaBrO_3 + 3CO_2$$
  
 $4NaBr + NaBrO_3 + 3H_2SO_4 \longrightarrow 3Na_2SO_4 + 3Br_2 + 3H_2O_3$ 

### EXAMPLE 4.5

An inorganic compound (X) gives a brick red flame on performing flame test. This compound gives the following tests also.

- a. Smells of chlorine when placed in moist air.
- **b.** If KI and CH<sub>3</sub>COOH are added to the suspension in water, a brown colour is obtained.

Identify (X) and write down equations for reactions at steps (a) and (b).

**Sol.** Compound (X) gives a brick red flame in flame test. Thus, it is a calcium compound. The smell of chlorine on exposure suggest that it is a bleaching powder. It is confirmed by reaction (b).

a. 
$$6\text{CaOCl}_2 \longrightarrow 5\text{CaCl}_2 + \text{Ca(ClO}_3)_2$$
  
 $\text{CaOCl}_2 + \text{CO}_2 \longrightarrow \text{CaCO}_3 + \text{Cl}_1 \uparrow$ 

**b.**  $CaOCl_2 + 2CH_3COOH \longrightarrow (CH_3COO)_2Ca + H_2O + Cl_2$  $2KI + Cl_2 \longrightarrow 2KCl + I_2$ 

### EXAMPLE 4.6

Gradual addition of KI solution to Bi(NO<sub>3</sub>)<sub>3</sub> solution initially produces a dark brown precipitate which dissolves in excess of KI to give a clear yellow solution. Write chemical equations for the above reactions.

**Sol.** Bi( $NO_3$ )<sub>3</sub> undergoes hydrolysis to produce nitric acid HNO<sub>3</sub> oxidises KI, i.e., I<sub>2</sub> (brown ppt.) is formed. The precipitated iodine dissolves in excess of KI and forms a yellow coloured solution of KI<sub>2</sub>.

$$Bi(NO_3)_3 + H_2O \longrightarrow Bi(OH)(NO_3)_2 + HNO_3$$

$$6KI + 8HNO_3 \longrightarrow 6KNO_3 + 2NO + 3I_2 + 4H_2O$$
Brown ppt.

$$KI + I_2 \longrightarrow KI_3$$
Yellow soln.

# EXAMPLE 4.7

Give reason: The brown colour of an acidified dilute solution of iodine in aqueous potassium iodide is intensified by addition

Nitrite ion being stronger oxidising agent than iodide ion,  $10 \longrightarrow 1_2$  and itself gets reduced to NO. Thus the brown intensified colour is intensified.

$$NO_2^{\ominus} + 2I^{\ominus} + 4H^{\oplus} \longrightarrow 2NO + I_2 + 2H_2O$$

Whereas sulphite is weaker oxidising agent than iodide and hence  $I_2$  is reduced to  $I^{\odot}$  and the solution becomes colourless or the brown colour is discharged.

$$I_2 + SO_3^{2-} + H_2O \longrightarrow SO_4^{2-} + 2H^{\oplus} + 2I^{\ominus}$$

# **Exercises**

## Single Correct Answer Type

# Physical and Chemical Properties of Halogens

- 1. Bond energy of halogens are
  - (1)  $F_2 > Cl_2 > Br_2 > l_2$
- (2)  $Cl_2 > Br_2 > F_2 > I_2$
- (3)  $Cl_1 > F_2 > Br_2 > I_2$
- (4)  $Br_2 > Cl_2 > F_2 > I_2$
- 2. IE of halogens are
  - (1) F > Cl > Br > l
- (2) Cl > F > Br > I
- (3) Cl > Br > I > F
- (4) Cl > Br > F > I
- 3. Which of the following does not liberate Br<sub>2</sub> from KBr?
  - $(1) I_{2}$

- (2) Cl<sub>2</sub>
- (3) conc.  $H_2SO_4$
- (4)  $F_2$
- 4. Which has the highest degree of hydrogen bonding?
  - (1) HCl

(2)  $H_2O$ 

(3) HF

- (4) HBr
- **5.** In case of halogens strong oxidising character is favoured by their
  - (1) Low dissociation energy
  - (2) Low E.A.
  - (3) Low IE
  - (4) Low hydration energy of  $X^{\Theta}$  ion
- **6.** Cl<sub>2</sub> is
  - (1) More reactive than F<sub>2</sub>
  - (2) Less reactive than Br<sub>2</sub>
  - (3) More reactive than  $Br_2$  and  $I_2$
  - (4) Less reactive than I<sub>2</sub>
- 7. The sum of energy term involved in the reaction:
  - $1/2 X_{2(g)} \longrightarrow X^{\Theta}_{(eq)}$  is highest in case of
  - (1) Flourine
- (2) Chlorine
- (3) Bromine
- (4) Iodine
- **8.** Which one of the following oxidises water to oxygen with large evolution of heat?
  - (1) Chlorine
- (2) Bromine
- (3) Iodine
- (4) Fluorine
- **9.** Which one of the following halogen acids has the lowest melting point?
  - (1) HF

(2) HCl

(3) HBr

- (4) HI
- **10.** Which of the following halogen acids has the highest boiling point?
  - (1) HF

(2) HCl

(3) HBr

- (4) HI
- 11. Size of the iodine species follows the order:
  - $(1) I^{\oplus} > I^{\ominus} > I$
- $(2) I > I^{\oplus} > I^{\Theta}$
- $(3) I > I^{\Theta} > I^{\oplus}$
- (4)  $I^{\odot} > I > I^{\oplus}$
- 12. Volatile nature of halogens is because
  - (1) The halogen molecules are more reactive

- (2) The force existing between the molecules are only weak van der Waal forces
- (3) Halogen molecules are bounded by strong forces
- (4) Halogen molecules are bounded by electrostatic forces
- 13. Which of the following will displace the halogen from the solution of the halide?
  - (1) Br<sub>2</sub> added to NaCl solution
  - (2) Cl<sub>2</sub> added to KCl solution
  - (3) Cl<sub>2</sub> added to NaF solution
  - (4) Br<sub>2</sub> added to KI solution
- 14. Which one of the following is the most basic?
  - (1)I

(2) Br

(3) Cl

- (4) F
- 15. On heating NaX with H<sub>2</sub>SO<sub>4</sub> and MnO<sub>2</sub> the halogens that cannot be prepared is \_\_\_\_\_.
  - $(1) I_2$

(2) Cl<sub>2</sub>

(3) Br<sub>2</sub>

- $(4) F_2$
- 16. In the reaction:

$$3Br_2 + 6OH^{\odot} \longrightarrow 5Br^{\odot} + BrO_3^{\odot} + 3H_2O, Br_2$$
 is

- (1) Oxidised
- (2) Reduced
- (3) Disintegrated
- (4) Disproportionated
- 17. Tincture of iodine contains
  - (1) I<sub>2</sub>, KI and C<sub>2</sub>H<sub>5</sub>OH
- (2)  $I_2$  and  $C_2H_5OH$
- (3) KI and  $C_2H_5OH$
- $(4) I_2 \text{ and } H_2O$
- 18. In the reaction  $I_2 + 2OH^{\ominus} \longrightarrow I^{\ominus} + IO^{\ominus} + H_2O$   $I_2$  is
  - (1) Oxidised
- (2) Reduced
- (3) Oxidised and reduced
- (4) Forms complex
- 19. Estimation of reducing substances by the use of standard L

$$I_2 + 2S_2O_3^{2-} \longrightarrow S_4O_6^{2-} + 2I^{\Theta}$$
 is called

- (1) Iodimetry
- (2) Iodometry
- (3) Oxidising
- (4) Reducing
- **20.** Estimation of oxidising substance involving the liberation of  $I_2$  and subsequent volumetric estimation of  $I_2$  are referred to as

$$2Cu^{2+} + 4I^{\Theta} \longrightarrow Cu_2I_2 + I_2$$
$$I_2 + S_2O_3^{2-} \longrightarrow S_4O_6^{2-} + 2I^{\Theta}$$

- (1) Iodimetry
- (2) Iodometry
- (3) Oxidising
- (4) Reducing
- 21. On passing Cl<sub>2</sub> water in a mixture of KBr and KI solution in contact with CCl<sub>4</sub> continuously with occasional shaking, we observe
  - (1) Orange CCl<sub>4</sub> layer changing to violet
  - (2) Persisting violet CCl<sub>4</sub> layer
  - (3) Persisting brown layer
  - (4) Violet layer changing into brown and finally colourless
- 22. When chlorine water is added to an aqueous solution of sodium iodide in the presence of chloroform, a violet

(2) Tincal

(2) Cl<sup>⊖</sup>

(4) I<sup>⊖</sup>

(2) Cl<sub>2</sub>

 $(4) I_2$ 

(2) CI

(4) F

(2) Oxygen

(4) Chlorine

(2)200

(4) 1000

(2) 136 pm

(4) 248 pm

**34.** Which halogen can be purified by sublimation?

What is the concentration of  $F^{\odot}$  in ppm?

(4) Carnallite

/	colouration is obtained. On a and vigorous shaking, the vishows the conversion of	idding more of chlorine water riolet colour disappears. This into
	hows the contract	(2) I <sub>2</sub> , HI
	(1) I <sub>2</sub> , HIO <sub>3</sub>	(4) I <sub>2</sub> , HOI
	(1) 12 (3) HI, HiO <sub>3</sub> The products of the chemical and H <sub>2</sub> O are	reaction between Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> , Cl <sub>2</sub>
	and 12 1) S. HCl, Na <sub>2</sub> SO <sub>4</sub>	(2) S, HCl, Na <sub>2</sub> S
	2) S HCl, Na <sub>2</sub> SO <sub>3</sub>	(4) S, NaClO,
24.	Fluorine on reaction with KIC with KHSO <sub>4</sub> gives (B). (A) an	2 gives (A) and on reaction
	(1) KIO <sub>4</sub> , K <sub>2</sub> S <sub>2</sub> O <sub>3</sub>	(2) KI, F <sub>2</sub> O
	NUE K.S.O.	$(4) I_2, K_2 S_2 O_8$
	$\operatorname{Br}_2 + \operatorname{OH}^{\Theta} \longrightarrow (A) + (B)$	2 6
	$(A) + (B) + H^{\oplus} \longrightarrow Br_2$	
	(A) gives yellow precipitate v	with AgNO <sub>3</sub> . (A) and (B) are
	$(1)$ Br $^{\Theta}$ , Br $O^{\Theta}$	$(2) \operatorname{Br}^{\Theta}, \operatorname{BrO}_{3}^{\Theta}$
	$(3)$ BrO $^{\ominus}$ , BrO $_3$	$(4) \operatorname{BrO}^{\Theta}, \operatorname{BrO}_4^{\Theta}$
26.	Which one of the following in fluorine and cold NaOH (dil.)	represents the reaction between 9?
	$(1) 2F_2 + 4NaOH \longrightarrow 4NaF$	$+2H_2O+O_2$
	$(2) 3F_2 + 6NaOH \longrightarrow 5NaF$	$+ \text{NaFO}_3 + 3\text{H}_2\text{O}$
	$(3) F_2 + 2NaOH \longrightarrow NaF + 1$	<u> </u>
	$(4) 2F_2 + 2NaOH \longrightarrow 2NaF$	$+ OF_2 + H_2O$
27.	Which one of the following poxygen when they react with	pairs of reactants does not form each other?
	(1) F <sub>2</sub> , NaOH solution (hot, o	conc.)

 $(2) F_2, H_2O$ 

(1) Ar

(3) Mg

(3) Cl<sub>2</sub>, NaOH solution (cold, dilute)

29. The colour of  $I_2$  is violet because it

(3) Absorbs yellow and green light

molecular weight, it is because

leading to higher stability

electrons per mole

(4) None of the above

of chlorine is

(1) Cu

 $(3) CuCl_2$ 

(1) Absorbs violet light

(4) None of the above

(2) Does not absorb light

(4) CaOCl<sub>2</sub>, H<sub>2</sub>SO<sub>4</sub> (dilute, small amount)

28. One atom of \_\_\_\_\_ combines with one atom of bromine.

30. The boiling points of halogens increase with increase in

(1) As the size increases molecules undergo association

(2) Bond strength increases due to increase in electronegativity

31. The catalyst used in the Deacon's process for the manufacture

(4) CuS

(2) An alloy of copper

(2) Rb

(4) HCl

39.	In the halogen group, chlorine is a gas, bromine is a liquid
	and iodine exists as solid crystals. Then the next halogen
	astatine (At) would be
	(1) Solid at room temperature

- (2) Having higher electronegativity
- (3) Liquid with higher ionisation enthalpy
- (4) Least atomic size

(1) Nitre

(1) F<sup>⊙</sup>

(3)  $Br^{\Theta}$ 

 $(1) F_{2}$ 

(3) Br<sub>2</sub>

(3) Br

(1) Ozone

(1)250

(3)400

(1) 272 pm

(3) 124 pm

(3) Fluorine

(3) Common salt

- **40.** Iodine is placed between two liquids C<sub>6</sub>H<sub>6</sub> and water:
  - (1) It dissolves more in C<sub>6</sub>H<sub>6</sub>
  - (2) It dissolves more in water
  - (3) It dissolves equally in both
  - (4) Does not dissolve in both
- **41.** Mixture of I<sub>2</sub> and sand can be separated by:
  - (1) Dissolving in water and filtering
  - (2) Fractional crystallisation
  - (3) Sublimation
  - (4) None of the above
- **42.** Which one is the strongest bond?
  - (1) Cl-F
- (2) F-F
- (3) Br-F
- (4) Br-Cl
- (3) van der Waals forces increase with increase in number of of oxides of halogens.
- 43. Which of the following trend correctly represents the stability
  - (1) I > Cl > Br(3) Br > Cl > I
- (2) Cl > I > Br
- (4) Br > I > Cl
- 44. Which is/are true statement(s)?
  - (1) The ionic character of M-X bond decreases in the order M-F > M-Cl > M-Br > M-I
  - (2) HI is strongest acid of HF, HCl, HBr and HI

- (3) Basic nature of  $X^{\odot}$  is in order  $F^{\odot} > Cl^{\odot} > Br^{\odot} > I^{\odot}$
- (4) All the above are correct statements
- 45. The three elements X, Y and Z with electronic configurations shown below all form hydrides:

Element	Electronic configuration
X	$1s^2 2s^2 2p^2$
Y	$1s^2 2s^2 2p^6 3s^1$
Z	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^2$

Which set of properties match correctly with properties of the hydrides of these elements:

	Hydride of X	Hydride of Y	Hydride Z
(1)	Colourles gas insoluble in H <sub>2</sub> O	Silver/grey solid reacts with H <sub>2</sub> O to form an alkaline solution.	Colourless gas forms a strong acid in H <sub>2</sub> O
(2)	Non-polar compound reacts with Cl <sub>2</sub> in light	Silver/grey ionic solid with formula YH <sub>2</sub>	Forms when water is added to phosphorus and elements Z.
(3)	Colourless gas which burns with air	Silver/grey solid which reacts violently with acids	Colourless, corrosive liquid at STP
(4)	Colourless liquid, no reaction with H <sub>2</sub> O	Silver/grey solid forms H <sub>2</sub> and H <sub>2</sub> O	Ionic solid with formula ZH

46. Bromine is commercially prepared from sea water by displacement reaction

$$Cl_2 + 2Br^{\odot} (aq) \longrightarrow 2Cl^{\odot} (aq) + Br_2$$

Br<sub>2</sub> gas thus formed is dissolved into solution of Na<sub>2</sub>CO<sub>3</sub> and then pure Br<sub>2</sub> is obtained by treatment of the solution with:

(1) HI

- (2) H<sub>2</sub>SO<sub>4</sub>
- (3) NaOH
- $(4) Ca(OH)_2$
- 47. Which of the following properties of halogens increase with increasing atomic number?
  - (I) Ionization energy
  - (II) Ionic radius
  - (III) Bond energy of the X<sub>2</sub> molecule
  - (IV) Enthalpy of vaporization
  - (1) I, II, III
- (2) I, III

(3) II, IV

- (4) IV
- 48. The high oxidizing power of fluorine is due to
  - (1) High heat of dissociation and high heat of hydration
  - (2) Low heat of dissociation and high heat of hydration
  - (3) High heat of dissociation and low heat of hydration
  - (4) High electron affinity
- 49. Affinity for hydrogen decreases in the group fluorine to iodine. Which of the halogen acids should have highest dissociation enthalpy?
  - (1) HF

(2) HCl

(3) HBr

(4) HI

- 50. Predict the correct product when Cl<sub>2</sub> passed through
  - H = O = O = H solution.
  - $(1) H^{\oplus} + Cl^{\odot} + O_2$  (both oxygen having 18)
  - (2) HOCl and HClO<sub>2</sub> (all oxygen having 18)
  - (3) HClO<sub>4</sub> and HCl (all oxygen having 18)
  - (4) Cl<sub>2</sub>O and H<sub>2</sub>O (all oxygen having 18)
- 51.  $Cl_2(g) + Ba(OH)_2 \longrightarrow X(aq.) + BaCl_2 + H_2O$  $X + H_2SO_4 \longrightarrow Y + BaSO_4$

$$Y \xrightarrow{\Delta \atop \Delta > 365 \text{ K}} Z + H_2O + O_2$$

Y and Z are respectively:

- (1) HClO<sub>4</sub>, Cl<sub>2</sub>O<sub>7</sub>
- (2) HClO<sub>3</sub>, ClO<sub>2</sub>
- (3) HClO<sub>3</sub>, ClO<sub>6</sub>
- (4) HClO<sub>4</sub>, ClO<sub>2</sub>
- 52. Cryolite and Caliche are the source of halogens A and  $\ensuremath{\mathtt{R}}$ respectively. A and B are
  - (1) Fluorine, Bromine
- (2) Sodium, Iodine
- (3) Fluorine, Iodine
- (4) Sodium, Bromine
- 53. Which of the following statements are correct for all three halogens (X), Cl, Br and I?
  - (1) They all form strong acid of the type HX
  - (2) They all need to gain one electron to acquire stable configuration
  - (3) Both (1) and (2) are correct
  - (4) None of the above is correct

### Compounds of Halogens

- 54. The oxidising ability of perhalates are in the order:

- (1)  $\text{ClO}_{4}^{\ominus} > \text{BrO}_{4}^{\ominus} > \text{IO}_{4}^{\ominus}$  (2)  $\text{ClO}_{4}^{\ominus} < \text{BrO}_{4}^{\ominus} < \text{IO}_{4}^{\ominus}$ (3)  $\text{BrO}_{4}^{\ominus} > \text{IO}_{4}^{\ominus} > \text{ClO}_{4}^{\ominus}$  (4)  $\text{IO}_{4}^{\ominus} < \text{BrO}_{4}^{\ominus} < \text{ClO}_{4}^{\ominus}$
- 55. Acid strength is in the order:
  - (1)  $HClO_4 > HIO_4 > HBrO_4$  (2)  $HClO_4 > HBrO_4 > HIO_4$
  - (3) HClO<sub>4</sub> < HBrO<sub>4</sub> > HIO<sub>4</sub> (4) None
- 56. Oxidising power of halogens are
  - (1)  $F_2 > Cl_2 > Br_2 > I_2 > At_2$  (2)  $At_2 > F_2 > Br_2 > Cl_2 > F_2$
  - (3)  $Cl_2 > Br_2 > F_2 > I_2 > At_2$  (4)  $Cl_2 > F_2 > Br_2 > I_2 > At_2$
- 57. Relative strength of acids are
  - (1) HF < HCl < HBr < HI
- (2) HF > HCl > HBr > HI
- (3) HCl < HF < HBr < HI
- (4) HI < HBr < HF < HI
- 58. Bond strength of halogen acids are
  - (1) HF > HCl > HBr > HI
- (2) HCl > HF > HBr > HI
- (3) HCl > HBr > HF > HI
- (4) HI > HBr > HCl < HF
- 59. Reducing properties of halogen acids are
  - (1) HF > HCl > HBr > HI
- (2) HF < HCl < HBr < HI
- (3) HCl > HF > HBr > HI
- (4) HCl > HBr > HF < HI
- 60. Which of the following halogen acid is a liquid?
  - (1) HF

(2) HCl

(3) HBr

(4) HI

- 61. Which of the following exists as an associated molecule even in the vapour state?
  - (1) HCl

(2) HBr

(3) HF

(4) HI

The relative acidic strength, stability and oxidising agent of the relative acidic strength, stability and oxidising agent of the relative acidic strength, stability and oxidising agent of and acids of chlorine are

 $\frac{\partial S}{\partial t} = \frac{\partial S}{\partial t} + \frac{\partial S}{\partial t} +$ 

 $\frac{\text{(IIII)}}{\text{(IIII)}} + \text{HCIO}_2 + \text{HCIO}_3 + \text{HOCI}$ 

(3) HOC1 < HClO<sub>2</sub> > HClO<sub>3</sub> > HClO<sub>4</sub>

(3)  $HClO_3 > HClO_2 > HClO_4 > HOCl$ 

In gaseous state, ionic character is greatest in

(1) HBr

(3) HCl

(4) HI

Mark the strongest reducing agent.

(1) H<sub>2</sub>F<sub>2</sub>

(2) HCl

(3) HBr

(4) HI

HCl and HF are prepared by heating their salt (NaCl and (aF<sub>2</sub>) with conc. H<sub>2</sub>SO<sub>4</sub> but HI and HBr cannot he prepared by similar reaction because HBr and HI have

(1) Reducing properties

(2) Oxidising property

(3) Complex forming ability (4) None of these

HBr and HI may be obtained by heating bromide and iodine with syrupy phosphoric acid not with H<sub>2</sub>SO<sub>4</sub> because H<sub>2</sub>SO<sub>4</sub>

(1) A weaker acid

(2) Less stable

(3) An oxidising agent

(4) A reducing agent

Mhich of the following is soluble in water?

(1) AgF

(2) AgBr

(3) AgCl

(4) AgI

A greenish yellow gas reacts with an alkali metal hydroxide to form a halate which can be used in fireworks and safety matches. The gas and the halate are

(1) Br<sub>2</sub>, KBrO<sub>3</sub>

(2) Cl<sub>2</sub>, KClO<sub>3</sub>

(3) I<sub>2</sub>, NaIO<sub>3</sub>

(4) I<sub>2</sub>, KIO<sub>3</sub>

 $\Theta. \text{ For } (A) + K_2 \text{CrO}_3 + \text{air} \xrightarrow{\text{Heat}} (B)$ 

 $(B) + Cl_2 \longrightarrow (C)$  pink

Which of the following is correct?

(1) (A) is black,  $MnO_2$ ; (B) is blue,  $K_2MnO_4$  and (C) is pink,

(2) (A) is green,  $Cr_2O_3$ ; (B) is yellow,  $K_2CrO_4$  and (C) is pink,  $K_2Cr_2O_7$ 

(3) (A) is black, MnO<sub>2</sub>; (B) is green, K<sub>2</sub>MnO<sub>4</sub> and (C) is pink, KMnO<sub>4</sub>

(4) (A) is black, Bi<sub>2</sub>O<sub>3</sub>; (B) is colourless, KBiO<sub>2</sub> and (C) is pink, KBiO<sub>2</sub>

70. Euchlorine is

(1) Obtained by heating perchlorate with conc. HCl

(2) A chloride of europium

(3) A mixture of  $Cl_2$  and  $Cl_2O_7$ 

(4) A mixture of Cl<sub>2</sub> and ClO<sub>2</sub>

71. Which is incorrectly matched?

 $\text{(1) } C_{S}Br_{3} \longrightarrow C_{S} ^{\oplus} + Br_{3} ^{\bigcirc} \longrightarrow C_{S} ^{\oplus} + Br_{2} ^{\bigcirc} + Br_{2}$ 

 $(2) I_4 O_9 \rightleftharpoons I^{3+} + 3(IO_3)^{\Theta}$ 

 $(3) \operatorname{AgBrO}_{3} \rightleftharpoons \operatorname{Ag}^{\oplus} \operatorname{Br}_{3}^{\ominus}$ 

 $(4) I_2 O_4 \rightleftharpoons IO_2^{\oplus} + IO_2^{\ominus}$ 

72. A certain compound (X) when treated with copper sulphate solution yields a brown precipitate. On adding hypo solution the precipitate turns white. The compound is

(1) K<sub>2</sub>CrO<sub>2</sub>

(3) KBr

 $(4) K_3 PO_4$ 

73.  $KClO_3$  on reaction with  $SO_2$  gives (A) and on reaction with conc. H<sub>2</sub>SO<sub>4</sub> gives (B). (A) and (B) are

(1) KCl, HClO<sub>4</sub>

(2) Cl<sub>2</sub>, ClO<sub>2</sub>

(3) KCl, HClO<sub>3</sub>

(4) Cl<sub>2</sub>, HClO<sub>4</sub>

74. 10 g of bleaching powder on reaction with KI required 50 mL of 2N hypo solution. Thus, % of bleaching powder

(1) 100

(2)80

(3)63.5

(4)35.5

75.  $HCIO_4 + P_2O_5 \longrightarrow (A) + (B)$ 

(A) and (B) are

(1) HClO<sub>3</sub>, H<sub>3</sub>PO<sub>4</sub>

(2) Cl<sub>2</sub>O<sub>6</sub>, HPO<sub>3</sub>

(3) ClO<sub>2</sub>, H<sub>3</sub>PO<sub>4</sub>

(4) Cl<sub>2</sub>O<sub>2</sub>, HPO<sub>3</sub>

 $AgClO_3 + (A) \longrightarrow (B) + (C) + (D)$ **76.** 

The substances (A), (B), (C) and (D) are

(1) Cl<sub>2</sub>, AgCl, ClO<sub>2</sub>, O<sub>2</sub>

(2) Cl<sub>2</sub>, Ag, Cl<sub>2</sub>O<sub>6</sub>, O<sub>2</sub>

(3) H<sub>2</sub>, AgCl, H<sub>2</sub>O, O<sub>2</sub>

(4) HClO, AgCl, ClO<sub>2</sub>, O<sub>2</sub>

77. Select the correct statement(s):

(1) Cl<sub>2</sub>O and ClO<sub>2</sub> are used as bleaching agents and as germicides.

(2) ClO<sub>2</sub> is the anhydride of HClO<sub>3</sub> and HClO<sub>3</sub>.

(3)  $I_2O_5$  is used in the quantitative estimation of CO.

(4) All of the above are correct.

**78.** Which bond has the greatest polarity?

(1) H-C1

(2) H-Br

(3) H-I

(4) H-F

79. Bleaching properties of bleaching powder are due to its

(1) Oxidising properties

(2) Reducing properties

(3) Basic properties

(4) Disinfecting properties

80. Bleaching powder is a mixture of

(1) Calcium hypochlorite and calcium chloride

(2) Calcium chlorate and calcium chloride

(3) Calcium hypochlorite and basic calcium chloride

(4) Calcium chlorate and calcium hydroxide

81. One can draw the map of a building on a glass plate by

(1) HI

(2) HF

(3) HBr

(4) HCl

82. The tetrahedral nature of the three bonds in a chlorate ion  $(ClO_3^{\Theta})$  is due to

(1) The presence of a lone pair of electrons

(2)  $sp^3$ -hybridisation

(3)  $sp^2$ -hybridisation

(4) Trigonal bipyramidal shape of ion

83. Which one of the following	owing acts as an antichlor?	93. In the preparation of HBr with H <sub>3</sub> PO <sub>4</sub> and not by co	or HI, NaX $(X = R_r)$
$(1) \text{ MnO}_2$	(2) Na2S2O3	with H <sub>3</sub> PO <sub>4</sub> and not by co	ncentrated H <sub>2</sub> SO <sub>4</sub> since
$(3) K_2 Cr_2 O_7$	(4) Na <sub>2</sub> SO <sub>4</sub>	(1) No D() is water incolu	hla 132
<b>84.</b> One gas bleaches the other by oxidation. The	e colour of flowers by reduction and nese gases are	(3) H <sub>2</sub> SO <sub>4</sub> oxidizes HX to	$X_2 (Br_2, I_2)$
(1) SO <sub>2</sub> and Cl <sub>2</sub>	(2) CO and Cl <sub>2</sub>	(4) H <sub>2</sub> SO <sub>4</sub> makes the react	ion reversible
$(3) NH_3$ and $SO_2$	(4) $H_2S$ and $Br_2$	<b>94.</b> The reaction of KMnO <sub>4</sub> ar	nd HCl results in
85. The following acids	have been arranged in the order of	(1) Reduction of Mn in KN	MnO, and production
decreasing acid streng	gth. Identify the correct order.	(2) Oxidation of Mill III KIV	mU <sub>4</sub> and production of '
ClOH(I) BrOH(II)	IOH(III)	(3) Reduction of Min in Ki	AnO <sub>4</sub> and production and
(1) I > II > III	(2) II > I > III	(4) Oxidation of Mn in KN	AnO <sub>4</sub> and production of Cl
(3) III > II > I	(4) I > III > II	95. $NaCl + A \longrightarrow NaNO_3 + B$	$B + Cl_2 + H_2O$
<b>86.</b> Which has maximum	pH in aqueous solution?	$B + O_2 \longrightarrow C + Cl_2$	-
(1) NaClO	(2) NaClO <sub>2</sub>	$C + O_2 + 2H_2O \longrightarrow A$	
(3) NaClO <sub>3</sub>	(4) NaClO <sub>4</sub>	A, B and C are	
	ough water to form a saturated solution.	(1) AgNO <sub>3</sub> , NaOCl, N <sub>2</sub> O <sub>4</sub>	(2) HNO <sub>3</sub> , NOCl, NO <sub>2</sub>
The aqueous solution	on treatment with AgNO <sub>3</sub> gives a white	(3) HNO <sub>3</sub> , NaOCl, NO	(4) AgNO <sub>3</sub> , NOCl, NO <sub>2</sub>
Mg ribbon with evol	rated aqueous solution also dissolves	96. The inter-halogen compoun	nd not obtained is
respectively:	ution of colourless gas Y, X and Y are	(1) BrCl <sub>7</sub>	(2) BrF <sub>5</sub>
(1) CO <sub>2</sub> ,Cl <sub>2</sub>	(2) Cl <sub>2</sub> , CO <sub>2</sub>	(3) IF <sub>5</sub>	(4) IC1
(3) Cl <sub>2</sub> , H <sub>2</sub>	(4) $H_2$ , $Cl_2$	97. Which of the underlined	l atoms in oxyacids have
88. Which one is the anhy		hybridized atoms?	4
(1) Cl <sub>2</sub> O <sub>7</sub>	(2) ClO <sub>2</sub>	(1) HClO <sub>4</sub> , HNO <sub>3</sub> , HClO <sub>3</sub>	4 2 4 1200;
$(3) \operatorname{Cl}_2 \operatorname{O}_6$	(4) Cl <sub>2</sub> O	(3) H2SO4, H2PO4, HNO3	$(4) \text{ HClO}_4, \text{ H}_2\text{SO}_4, \text{ HNO}_2$
89. Which of the follow	ing is not the characteristic of inter-	98. Auto oxidation of bleaching	
halogen compounds?		(1) Only calcium chlorate	(2) Only calcium hypochlorid
(1) They have low bo	iling points and are highly volatile	(3) Only calcium chloride	(4) Both (1) and (3)
(2) They are covalent		99. Which is incorrectly match	
(3) They are quite uns	stable but none of them is explosive	$(1) I_4 O_9 \rightleftharpoons I^{3+} + 3IO_3^{\odot}$	$(2) \operatorname{CsBr}_{\mathfrak{Z}} \rightleftharpoons \operatorname{Cs}^{\oplus} + \operatorname{Br}_{\mathfrak{Z}}^{\oplus}$
(4) They are more rea	ctive than halogens	$(3) I_2O_4 \rightleftharpoons IO^{\oplus} + IO_3^{\ominus}$	(4) None of these
4. Then incorrect star	Is $HClO_n$ series, here value of $n$ is 1 to	<b>100.</b> The incorrect order is:	
(1) 'Cl—O' bond orde	tement regarding these oxy acids is: $\frac{n}{n}$ decreases with decreasing value of $n$ .	(1) HF > HC1 > HBr > HI: I	Bond dissociation enthalpy
(2) Thermal stability	of oxy acids decreases with increasing	(2) HF > HCl > HBr > HI: I	Boiling point
value of n.		(3) $HF > HCl > HBr > HI$ :	Thermal stability
(3) Oxidizing power of	of oxy acids increases with decreasing	(4) $HF < HCl < HBr < HI$ : A	
value of <i>n</i> .  (4) Acidic character of	f oxy acids increases with increasing	101. Concentrated H <sub>2</sub> SO <sub>4</sub> cannot NaBr, because it:	
value of n.	_	<ul><li>(1) reacts slowly with NaBr</li><li>(3) Oxidises HBr</li></ul>	
<b>91.</b> In, $\text{Cl}_2\text{O}_6(l) + \text{HF}$			(4) Reduces HBr
hybridization of Cl-ato	ches with Q, then correct option for om and ∠OCIO in the P and Q ions:	102. A greenish yellow gas react to form a halite which can matches. The gas and halite	be used in fire works and safer,
	(2) Q: $sp^3$ ; 109°28′	(1) Br <sub>2</sub> , KBrO <sub>3</sub>	(2) Cl <sub>2</sub> , KClO <sub>3</sub>
	(4) P: $sp^1$ ; $\geq 120^\circ$	(3) I <sub>2</sub> , NaIO <sub>3</sub>	(4) None
	egarding $ClO_n^{\ominus}$ molecular ion is:	103. Which of the following is an	
increase	e of n, hybrid orbitals on central atom	halogen analogues of inter- $(1) C_2 N_2$	nalogen)? (2) BrF <sub>5</sub>
	e of $n$ , oxidation number of central	(3) ICN	(4) HSCN
	of 'n', 'Cl—O' bond length increases of 'n', 'Cl—O' bond order increases	104. A dark violet solid X rea explosive which decomposing gas. X also reacts with H <sub>2</sub> to prepared by heating its salt with the prepared by heati	o give an acid Y. Y can also be

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- (2) SO<sub>2</sub>, H<sub>2</sub>SO<sub>4</sub>
- (3) Br<sub>2</sub>, HBr
- $(4) I_2, HI$

105. In the reaction,  $\frac{3Br_2 + 6CO_3^{2-} + 3H_2O \longrightarrow 5Br^{\odot} + BrO_3^{\odot} + 6HCO_3^{\odot}}{3Br_2 + 6CO_3^{\odot} + 6HCO_3^{\odot}}$ 

- (1) Bromine is neither oxidized nor reduced
- (2) Bromine is both oxidized and reduced
- (3) Bromine is reduced and water is oxidized
- (4) Bromine is oxidized and carbonate is reduced

Which of the following does not decolourise iodine?

- (1)  $Na_2$   $SO_3$
- (2) NaCl
- $(3) Na_2S_2O_3$
- (4) NaOH

107. Ammonia and chlorine are made to react. If ammonia is in excess, products formed are A and B and when chlorine is in excess the products are C and D. A, B, C and D are

- (1) N<sub>2</sub>, NH<sub>4</sub>Cl and NCl<sub>3</sub>, HCl
- (2) N<sub>2</sub>, HCl and N<sub>2</sub>, NH<sub>4</sub>Cl
- (3) N<sub>2</sub>, NH<sub>4</sub>Cl and NCl<sub>3</sub>, HCl
- (4) NCl<sub>3</sub>, HCl and N<sub>2</sub>, NH<sub>4</sub>Cl

108. Inter-halogen compound which exists in dimeric form, is:

(1) ICl<sub>3</sub>

(2) IC1

(3) IF<sub>7</sub>

(4) BrF<sub>5</sub>

### Multiple Correct Answers Type

# Physical and Chemical Properties of Halogens

1. Which one of the following arrangements does not give the correct picture of the trends indicated against it?

- (1)  $F_2 > Cl_2 > Br_2 > I_2$
- : Bond dissociation energy
- (2)  $F_2 > Cl_2 > Br_2 > I_2$
- : Oxidising power
- (3) F > C1 > Br > I
- : Electron gain enthalpy
- $(4) F_{2} > Cl_{2} > Br_{2} > I_{2}$
- : Electronegativity

2. Which one of the following halogens turn(s) starch iodide paper blue?

(1) Cl<sub>2</sub>

(2)  $Br_2$ 

 $(3) I_{2}$ 

 $(4) F_{2}$ 

3. Which one of the following salts will evolve halogen on treatment with conc. H<sub>2</sub>SO<sub>4</sub>?

- (1) NaCl
- (2) CaCl<sub>2</sub>
- (3) NaBr
- (4) KI

4. Electrolysis of aqueous solution of Brine (NaCl) gives

(1) Cl<sub>2</sub>

- $(2) H_2$
- (3) NaOH
- (4) None of these

5. The halogens, which are not attacked by conc. HNO<sub>3</sub>, are

 $(1) F_{2}$ 

- (2) Cl<sub>2</sub>
- (3) Br<sub>2</sub>

 $(4) I_2$ 

6. Select the correct order:

- (1) HI > HBr > HCl > HF
- (2) HClO<sub>4</sub> > HBrO<sub>4</sub> > HIO<sub>4</sub>
- (3) HClO < HBrO < HIO
- (4) None of these

7. Which one of the following reactions does not occur?

- $(1) F_2 + 2Cl^{\Theta} \longrightarrow 2F^{\Theta} + Cl_2 (2) Cl_2 + 2F^{\Theta} \longrightarrow 2Cl^{\Theta} + F_2$
- $(3) Br_2 + 2I^{\Theta} \longrightarrow 2Br^{\Theta} + I_2 \quad (4) I_2 + 2Br^{\Theta} \longrightarrow Br_2^{\Theta} + 2I^{\Theta}$

- 8. Identify the correct statements:
  - (1) SCN<sup>⊙</sup> is a pseudohalide
  - (2) Iodine shows Lewis basic nature
  - (3) AgF is insoluble in water
  - (4) Fluorine is a super halogen
- 9. Which of the following properties of the elements chlorine, bromine and iodine increases with increasing atomic number?
  - (1) Enthalpy of vaporization
  - (2) Ionic radius
  - (3) Bond energy of the molecule  $X_2$
  - (4) Ionization energy
- 10. Predict product(s) in the following reaction

$$Cl_2 + OH \xrightarrow{\bigcirc} ?$$

- $(1) ClO_3^{\odot}$
- (2) OC1<sup>©</sup>
- (3) ClO<sub>3</sub> <sup>3</sup> <sup>9</sup>
- (4) Cl<sup>⊙</sup>

11. Which of the following statement(s) is/are correct for Halogens?

- (1) The strongest oxidizing agent is iodine
- (2) The most reactive halogen is fluorine
- (3) The most electronegative element is fluorine
- (4) Halogen which is liquid at room temperature is bromine
- 12. Select the correct statement(s)
  - (1) Chile saltpeter (NaNO<sub>3</sub>) is a main source of I<sub>2</sub>
  - (2)  $\mathrm{IO_3}^{\odot}$  is reduced to  $\mathrm{I}^{\odot}$  and which in turn oxidized to  $\mathrm{I}_2$  by IO₃ in acidic medium
  - (3) Anhydrous HF is a non-conduct of electricity
  - (4) F<sub>2</sub> is obtained by electrolysis of molten KHF<sub>2</sub>
- 13. Select the incorrect statement(s)
  - (1) NF3 has a highest dipole moment among CO, NH3 and
  - (2) HClO<sub>3</sub> is weakest acid among HIO<sub>3</sub>, HBrO<sub>3</sub> and HClO<sub>3</sub>
  - (3) Cl<sub>2</sub> has a lowest boiling point among Cl<sub>2</sub>, Br<sub>2</sub> and I<sub>2</sub>
  - (4) HF has a highest boiling point among CH<sub>4</sub>, NH<sub>3</sub> and HF

$$\frac{1}{2}F_2 + e^- \longrightarrow F^- \qquad E^\circ = 2.87 \text{ V}$$

14. Base on the values given, select correct statements

$$\frac{1}{2}\text{Cl}_2 + e^- \longrightarrow \text{Cl}^- \qquad E^\circ = 1.40 \text{ V}$$

$$\frac{1}{2}Br_2 + e^- \longrightarrow Br^- \qquad E^\circ = 1.09 \text{ V}$$

$$\frac{1}{2}I_2 + e^- \longrightarrow I^- \qquad E^\circ = 0.62 \text{ V}$$

- (1) Oxidizing power is in order  $F_2 < Cl_2 < Br_2 < I_2$
- (2) Oxidizing power is in order  $F_2 > Cl_2 > Br_2 > I_2$
- (3) Oxidizing power of I<sub>2</sub> is maximum
- (4) Oxidizing power of F<sub>2</sub> is maximum
- 15. All the halogens are coloured and the colour changes with increasing size of the halogen molecule. It is due to
  - (1) adsorption of light in the visible region

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- (2) transition from  $\pi^*$  to  $\sigma^*$  molecular orbital
- (3) transition from  $\pi$  to  $\pi^*$  molecular orbital
- (4) none of these
- 16. In correct statements about the hydrogen halides include
  - (1) They are all coloured
  - (2) The thermal stability decreases with increasing atomic number of halogen
  - (3) They all form soluble silver salts
  - (4) They all donate protons to water
- 17. Select the correct statement(s)
  - (1)  $pK_a$  value of HI (strongest halogen acid) is most negative
  - (2) High H-F bond strength makes H-F a weak acid in dilute aqueous solution
  - (3) Halogen forms clathrates by freezing solution in water
  - (4)  $K_a$  values of HX is in order HF < HCl < HBr < HI
- 18. Which of the following arrangements represent correctly the property indicated against it.
  - (1) Br < Cl < F: Electron affinity
  - (2)  $Br_2 < Cl_2 < F_2$ : Oxidizing power
  - (3) Br < Cl < F: Electronegativity
  - (4)  $Br_2 < Cl_2 < F_2$ : Bond energy
- 19. In the isolation of fluorine a number of difficulties were encountered. Which statements are correct?
  - (1) Fluorine reacts with moist glass vessels
  - (2) Fluorine has great affinity for hydrogen
  - (3) Electrolysis of aqueous HF gives ozonized oxygen
  - (4) The potential required for the discharge of the fluoride ions lowest
- 20. Iodine is formed when potassium iodide reacts with:
  - (1) ZnSO,
- (2) CuSO<sub>4</sub>

(3) Cl<sub>2</sub>

- (4) Br<sub>2</sub>
- 21. Select the correct order(s)
  - (1) HOCl > HOBr > HOI acid strength
  - (2)  $HCIO_4 < HCIO_3 < HCIO_2 \le HCIO oxidizing power$
  - (3)  $ClO_4^- < BrO_4^- > IO_4^- oxidizing power$
  - (4) IO<sup>-</sup> > BrO<sup>-</sup> > ClO<sup>-</sup> ease of disproportionation
- 22. Select the correct ones
  - (1) BrO<sub>2</sub> upon alkaline hydrolysis gives bromide and bromate
  - (2) It converts benzene to 1,4-diquinone
  - (3) It converts  $I_2$  to  $I_2O_5$
  - (4) Br<sub>2</sub>O is a dark brown solid and is highly oxidizing
- 23. Iodine reacts with hypo to give:
  - (1) NaI

- (2)  $Na_2S_4O_6$
- (3) Na<sub>2</sub>SO<sub>3</sub>
- $(4) \text{ Na}_2 \text{SO}_4$
- 24. Chlorine reacts with
  - $(1) N_{2}$

(2)  $O_2$ 

(3)  $S_{8}$ 

- (4) Fe
- 25. Which oxidation state of Cl is observed when Cl<sub>2</sub> reacts with hot and conc. NaOH solution?
  - (1)+1

(2)-1

(3) + 5

(4)+7

- 26. If Y<sub>2</sub> in given reaction is Cl<sub>2</sub> then "X" is/are:
  - (1)I

(2) Br (4) F

- (3) C1
- $Y_2 + 2X_{(aq.)}^{\odot} \longrightarrow 2Y_{(aq.)}^{\odot} + X_2$
- 27. Available chlorine is liberated from bleaching powder  $_{Wh_{e_\eta}}$ 
  - (1) reacts with CO<sub>2</sub>
- (2) reacts with acid
- (3) reacts with H<sub>2</sub>O
- (4) is heated
- 28. Species which are isoelectronic with OF, are
  - (1) ClO<sup>⊙</sup>

(2) CIF

(3) ClO<sub>3</sub>

- (4) ClO<sub>2</sub>
- 29. HI cannot be prepared by the action of conc.  $H_2SO_4$  on k
  - (1) HI is stronger acid than H<sub>2</sub>SO<sub>4</sub>
  - (2) H<sub>2</sub>SO<sub>4</sub> is stronger oxidising agent than HI
  - (3) H<sub>2</sub>SO<sub>4</sub> is an oxidising agent
  - (4) HI is a strong reducing agent
- 30. Select triangular planar species among the following:
  - $(1) ClO_3^{\Theta}$
- (2) H<sub>3</sub>O<sup>⊕</sup>

(3) CH<sub>2</sub><sup>⊕</sup>

- (4) ClO,<sup>⊕</sup>
- 31. Iodine reacts with hypo to give
  - (1) NaI

- (2) Na<sub>2</sub>SO<sub>2</sub>
- $(3) \text{ Na}_{2} \text{S}_{4} \text{O}_{6}$
- (4) Na, SO,
- 32. Which one of the following are pseudohalide ions?
  - (1)  $CNO^{\Theta}$
- (2) OCN<sup>⊖</sup>
- (3)  $RCOO^{\Theta}$
- $(4) N_2^{\Theta}$
- 33. Cl<sub>2</sub> reacts with hot aqueous NaOH to give
  - (1) NaCl
- (2) NaClO<sub>2</sub>
- (3) NaClO<sub>2</sub>
- (4) NaClO,
- 34. Aqueous solution of Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> on reaction with Cl<sub>2</sub> gives (1)  $Na_{2}S_{4}O_{6}$ (2) NaHSO,

(3) HCl

- (4) NaOH
- 35. Which of the following statements are correct?
  - (1) Bleaching powder converts acetone or ethyl alcohol into chloroform
  - (2) The maximum percentage of available chlorine calculated from odling's formula is 49%
  - (3) Thermal stability of  $KI_3^{\circ} \le Nal_3^{\circ}$
  - (4) Thermal stability for trihalides formed by same metal is
  - $I_3^{\odot} \ge IBr_2^{\odot} \ge ICl_2^{\odot} \ge I_2Br^{\odot} \ge Br_3^{\odot} \ge BrCl_2^{\odot} \ge Br_2Cl_2^{\odot}$
- 36. Hypoiodous acid is formed with
  - (1) KOH

- (2) HgO
- (3) C<sub>2</sub>H<sub>2</sub>OH
- $(4) I_{2}$
- 37. Which of the following product(s) is/are obtained when Cl<sub>2</sub>O<sub>6</sub> reacts with NaOH?
  - (1) KCIO<sub>4</sub>
- (2) KClO<sub>3</sub>
- (3) KClO,
- (4) KCI
- 38. Which of the following species does/do not exist?
  - (1) ICl₃<sup>⊕</sup>

(2) NCl<sub>5</sub>

- (3) NH<sub>2</sub><sup>⊕</sup>
- $(4) OF_{4}$

The possible product(s) formed in the following reaction is/

 $_{\text{lf}_5}^{\text{"}} + \text{H}_2\text{O} \longrightarrow ?$ 

(2) HIO,

(3) HIO

(4) HIO<sub>3</sub>

Which of the following reaction(s) do/does not give an oxo-

<sub>(1)</sub> Two moles of nitric and  $\xrightarrow{-H_2O}$ 

(2) One mole of sulphurus acid  $\xrightarrow{-H_2O}$ 

(3) Two moles of per chloric acid ——H<sub>2</sub>O

 $_{(4)}$  Two moles of sulphuric acid  $\xrightarrow{-H_2O}$ 

#. Correct order(s) is/are:

(1)X – C – N bond angle:  $COCl_2 > COF_2$ 

 $\frac{(1)}{(2)}$  Melting point: NH<sub>3</sub> < SbH<sub>3</sub> < AsH<sub>3</sub> < PH<sub>3</sub>

3) Bond dissociation energy:  $Cl_2 > Br_2 > F_2 > I_2$ 

(4) Thermal stability:  $H_2O > H_2S > H_2Se > H_1Te$ 

Which reactions are used for the preparation of the halogen

$$(1) \ 2KI + H_2SO_4 \longrightarrow K_2SO_4 + 2HI$$

$$(conc.)$$

(2) 
$$CaF_2 + H_2SO_4 \longrightarrow CaSO_4 + 2HF$$

$$(3) \ \ NaCl + H_2SO_4 \longrightarrow NaHSO_4 + HCl$$

$$(conc.)$$

(4) 
$$2KBr + H_2SO_4 \longrightarrow K_2SO_4 + 2HBr$$

43. Which of the following statements are correct?

- (1) Fluorine compounds are more stable than corresponding chlorine compounds
- (2) Fluorine forms oxysalt when it react with alkalies while other halogens do not
- (3) F<sub>2</sub> undergoes disproportionation reaction in the alkaline medium while other halogens do not
- (4) Due to hydrogen bonding HF can form acid salts of the type  $[K^{\dagger}(F-H-F)^{-}]$
- 44. Which of the following statement(s) is/are correct?
  - (1) ClO<sub>2</sub> is a yellow gas but deep red liquid
  - (2) ClO<sub>2</sub> is diamagnetic in nature
  - (3) ClO<sub>2</sub> in alkaline solution undergoes disproportionation
- (4) Chlorine dioxide (ClO<sub>2</sub>) is powerful oxidizing agent but bleaching action is lower than Cl<sub>2</sub>
- 45. Which of the following statements is true about NO2 and
  - (1) In both oxides, the central atom has an oxidation state +4
  - (2) On cooling, both undergoes dimerization
  - (3) Both have a bent structure
  - (4) Both are paramagnetic
- $^{46}$ ,  $Cl_2O_6 + NaOH \longrightarrow ?$ (1) NaClO<sub>3</sub>
- (2) NaClO<sub>2</sub>
- (3) NaOCl
- (4) NaClO<sub>4</sub>

- 47. Select the
  - (1)  $F_2$  form  $F_3^{\odot}$  ion and  $I_2$  form  $I_3^{\odot}$  ion
  - (2) CIF<sub>3</sub> exists but FCl<sub>3</sub> does not
  - (3) Alkaline KMnO<sub>4</sub> oxidises I<sub>2</sub> to I<sup>⊙</sup>
  - (4) F<sub>2</sub> forms only one oxo acids.
- **48.** Select the incorrect statements
  - (1) Both NO and ClO<sub>2</sub> dimerises
  - (2) Addition of excess of Cl<sub>2</sub> to KI solution gives colourless solution
  - (3)  $H_2SO_4$  is stronger acid than  $HClO_4$
  - (4) Inter-halogen compounds are more reactive than halogens

### **Linked Comprehension Type**



### Paragraph 1

Fluorine, the first member of group 17, differs from the other members of the group in many respects due to:

- i. Very small size
- ii. Very high electronegativity
- iii. Absence of vacant d-orbitals in the valence shell
- iv. Dissociation energy in the molecular form  $(X_2)$  is the least
- 1. Which member of the group 17 does not show positive oxidation state?
  - (1) Iodine
- (2) Bromine
- (3) Chlorine
- (4) Fluorine
- 2. Which has the maximum molar enthalpy of vaporisation?
  - (1) HF

(2) HC1

(3) HBr

- (4) HI
- 3. Which of the following bonds is the strongest?
  - (1) F F
- (2) Cl—Cl
- (3) Br—Br
- (4) I—I
- 4. Which halogen does not form any oxyacid?
  - (1) Iodine
- (2) Bromine
- (3) Chlorine
- (4) Fluorine
- 5. The most basic among the following is:
  - (1) Cl<sup>Θ</sup>

 $(2) \operatorname{Br}^{\Theta}$ 

(3) F<sup>⊖</sup>

- (4) I<sup>⊖</sup>
- 6. Which of the following do not exist?
  - (1) IF

(2) FCl<sub>3</sub>

(3) IF<sub>3</sub>

(4) IF<sub>5</sub>

### Paragraph 2

Halogens react with each other to form a number of compounds called interhalogen compounds. Their general formula is AX, where A is less electronegative halogen while X is a more electronegative halogen and n is its number. The interhalogen compounds are essentially covalent and more reactive than the halogens since the bond A-X is weaker than A-A or X-X bond. The reactions of interhalogens are similar to those of halogens.

- 7. Which of the following interhalogen compound is not possible?
  - (1) IF<sub>7</sub>

(2) IF<sub>5</sub>

(3) ClF<sub>3</sub>

(4) FBr<sub>3</sub>

### 4.42 Inorganic Chemistry

- 8. Which halogen shows maximum oxidation state in forming interhalogen compound?
  - (1)I

(2) Br

(3) Cl

- (4) F
- 9. How many lone pairs of electrons are present on chlorine in ClF<sub>3</sub> molecule?
  - (1)0

(2)1

(3)2

- (4)3
- 10. Which of the following statement is wrong for inter-halogen?
  - (1) The value of n in  $AX_n$  (interhalogen) can be 1, 3, 5 or 7
  - (2) The value of n in AX, (interhalogen) can be 2, 4, or 6
  - (3) A can never be fluorine as it is most electronegative halogen.
  - (4) X can never be iodine as it is least electronegative halogen.

### Paragraph 3

I, has less solubility in water and its solubility increases on adding  $\bar{\text{KI}}$  solution. When KI and  $I_2$  react then a species 'X' is formed by which solubility of I<sub>2</sub> increases.

- 11. Hybridisation of anionic part of 'X' is
  - $(1) sp^2$

- $(3) sp^3 d$
- $(4) sp^3d^2$
- 12. Shape of anionic part of 'X' is
  - (1) Linear
- (2) T shape
- (3) Pyramidal
- (4) See-saw
- 13. Which of the following is the correct characteristic of anionic part of 'X'?

[Polar and non-polar nature to be considered on the basis of dipole moment]

- (I) Planar
- (II) non-planar
- (III) Polar (IV) non-polar
- (1) I and III
- (2) I and IV
- (3) II and III
- (4) II and IV
- 14. Geometry of anionic part of X is
  - (1) Trigonal bipyramidal
- (2) Square pyramidal
- (3) Pentagon
- (4) Linear

### Paragraph 4

Oxygen is more electronegative than chlorine. In the series of oxyacids HOCl, HClO<sub>2</sub>, HClO<sub>3</sub> and HClO<sub>4</sub>, an increasing number of oxygen atom is bonded to the chlorine atom.

Chlorine forms a number of oxyacids which differ in their strengths. The conjugate base of these acids also differs in their stability order.

- 15. The order of acidic strength of HOCl, HClO<sub>2</sub>, HClO<sub>3</sub> and HClO<sub>4</sub> are
  - (1) HClO<sub>4</sub> > HClO<sub>3</sub> > HClO<sub>2</sub> > HOCl
  - (2) HOCl > HClO<sub>2</sub> > HClO<sub>3</sub> > HClO<sub>4</sub>
  - (3) HClO<sub>3</sub> > HClO<sub>4</sub> > HClO<sub>2</sub> > HOCl
  - (4) HClO<sub>3</sub> > HClO<sub>2</sub> > HOCl > HClO<sub>4</sub>
- 16. Which of the following is the strongest conjugate base?
  - (1) ClO<sup>⊖</sup>

- (3) ClO<sub>3</sub><sup>⊖</sup>
- (2) ClO<sub>2</sub> ⊖ (4) ClO<sub>4</sub> ⊖

- 17. The hybridisation of Cl in ClO<sub>2</sub> and its shape are
  - (1)  $sp^3$ , pyramidal
- (2)  $sp^2$ , angular
- (3)  $sp^3$ , angular
- (4)  $sp^2$ , trigonal planar
- 18. The least stable oxo-anion among the following is
  - (1) ClO<sup>⊖</sup>
- (3) CIO<sub>1</sub><sup>©</sup>
- (4) ClO<sub>4</sub><sup>⊙</sup>

### Paragraph 5

Among the halogens, fluorine differs considerably from the other members. The hydrides of halogens also differ in their properties

- 19. Fluorine differs from the other halogens due to:
  - (1) Small size
  - (2) Very high electronegativity
  - (3) Non-availability of d-orbitals
  - (4) All of these
- 20. Which of the following bond has the highest bond energy?
  - (1) F F

- (2) Cl-Cl
- (3) Br–Br
- (4) I I
- 21. Which of the following halogens do not form polyhalide?
  - (1) F

(2) C1

(3) Br

(4) I

### Paragraph 6

Bleaching powder is a mixed salt of hydrochloric acid and hypochlorous acid. It has the formula, CaOCl, H,O. It is manufactured by the action of chlorine on dry slaked lime at 40°C There is also a view that bleaching powder is a mixture of calcium hypochlorite and basic calcium chloride,

 $[Ca(OCl)_2 + CaCl_2 \cdot Ca(OH)_2 \cdot H_2O].$ 

The amount of chlorine obtained from a sample of bleaching powder by the treatment with excess of dilute acids or CO<sub>2</sub> is called available chlorine. A good sample of bleaching powder contains 35-38% of available chlorine. On long standing, it undergoes auto-oxidation and the amount of available chlorine decreases. The estimation of available chlorine is done volumetrically by iodometric method or by (b) arsenite method.

In textile industry, the cotton cloth is mainly bleached with the help of bleaching powder.

- 22. Maximum percentage of available chlorine on the basis of CaOCl<sub>2</sub>·H<sub>2</sub>O formula is
  - (1)35

(2)40

(3)45

(4)49

11.

- 23. On long standing, the bleaching powder undergoes autooxidation. The products formed are
  - (1) Calcium chloride only
  - (2) Calcium chlorate only
  - (3) Calcium chloride and calcium chlorate
  - (4) Calcium chloride and calcium chlorite
- 24. The chemical name of bleaching powder is
  - (1) Calcium hypochlorite
  - (2) Calcium chlorohypochorite
  - (3) Calcium chlorate
  - (4) Calcium perchlorate

The percentage of available chlorine in commercial samples of bleaching powder is usually between 35% and 28% the percentage of blenching powder is usually between 35% and 38%. The ow value is due to

 $\log \frac{\log V_{\rm plane}}{\log \log V_{\rm plane}}$  is formation. its formation.

Impurities present in the original slaked lime. (3) Decomposition of bleaching powder when kept in air. (4) All of the above.

13.55 g of bleaching powder when treated with acetic acid and 15.55 g of KI liberated iodine which required 60. 3.55 g of K1 liberated iodine which required 60 mL of 0.5 N sodium thiosulphate solution. The percentage of available chlorine in the sample is

 $(1)^{30.0}$ 

(2) 25.0

(3) 20.0

(4) 35.0

# Natrix Match Type

is section contains questions each with two columns—I and II. the items given in column I with that in column II.

13	Column I	ndos:	Column II
9.	I <sub>2</sub> O <sub>5</sub>	i.	Liquid at room temperature
0.	ClO <sub>2</sub>	ii.	Used in estimation of CO
	Br <sub>2</sub>	iii.	Paramagnetic
1.	O <sub>2</sub>	iv.	Powerful bleaching agent

	Column I	900	Column II
a.	I <sup>⊙</sup>	i.	Pseudo halide
b.	CN <sup>⊙</sup>	ii.	Gives compound with Cu <sup>+2</sup> via redox reaction
c.	HClO <sub>4</sub>	iii.	Reacts with HF
d.	HOC1	iv.	Acid anhydride

	Column I		Column II
<b>a.</b>	Deacon process	i.	Isolation of F <sub>2</sub>
b.	Baeyer process	ii.	Manufacture of HNO <sub>3</sub>
c.	Moissan method	iii.	Manufacture of Cl <sub>2</sub>
d.	Ostwald process	iv.	Purification of bauxite

	Column I		Column II
a.	Corrosive liquid	i.	F <sub>2</sub>
b.	Maximum solubility in water	ii.	Cl <sub>2</sub>
c.	Maximum bond dissociation energy	iii.	Br <sub>2</sub>
d.	Maximum inter-atomic distance	iv.	I <sub>2</sub>

	Column I		Column II
a.	Bleaching powder	i.	HF
b.	Pseudohalogen	ii.	IBr <sub>3</sub>
c.	Interhalogen compound	iii.	(CN) <sub>2</sub>
d.	Hydrogen bonding	iv.	CaOCl <sub>2</sub>

(Int	Column I cerhalogen compound)	(	Column II (Hybridisation of I)
a.	ICI	i.	$sp^3d$
b.	ICl <sub>3</sub>	ji.	$sp^3d^3$
c.	ICl <sub>5</sub>	iii.	$\mathrm{sp}^{3}\mathrm{d}^{2}$
d.	ICl <sub>7</sub>	iv.	sp <sup>3</sup>

Column I		Column II	
a.	Fluorspar	i.	Na <sub>3</sub> AlF <sub>6</sub>
b.	Cryolite	ii.	AgC1
c.	Apatite	iii.	CaF <sub>2</sub>
d.	Horn silver	iv.	MgCl <sub>2</sub> ·KCl·6H <sub>2</sub> O

	Column I	Column II		
a.	Carnalite	i.	KCl	
b.	Sylvine	ii.	Ash obtained on burning sea-weeds which contains 1% iodine as iodine of alkali metal	
c.	Kelp	iii.	KCl·MgCl <sub>2</sub> ·6H <sub>2</sub> O	
d.	Caliche	iv.	Contains iodine as sodium iodate	

9.		Column I	An area of the	Column II
	a.	HOCl	i.	Perhalic acid
	b.	HClO <sub>2</sub>	ii.	Halous acid
	c.	HClO <sub>3</sub>	iii.	Hypohalous acid
	d.	HClO <sub>4</sub>	iv.	Halic acid

10.		Column I		Column II
	a.	Fermy's salt	i.	KClO <sub>3</sub>
	b.	Javelle water	ii.	KHF <sub>2</sub>
	c.	Berthelot's salt	iii.	Aqueous solution of NaOCl
	d.	Anhydrone	iv.	Anhydrous magnesium perchlorate

II. Match the items given in Column I with that in Column II and III

Column I	Column II		Column III		
Interhalogen compound		Characteristics (I)		Characteristics (II)	
IF	i.	Undergo hydrolysis to give periodic acid	p.	$sp^3d$ , arrow shape, 2 $lp$	
IF <sub>3</sub>	ii.	Undergo hydrolysis to give hypoiodous acid	q.	$sp^3$ , linear, $3 lp$	
IF <sub>5</sub>	iii.	Undergo hydrolysis to give iodous acid	r.	$sp^3d^3$ , pentagonal bipyramidal, zero $lp$	
IF <sub>7</sub>	iv.	Undergo hydrolysis to give iodic acid	s.	$sp^3d^2$ , square pyramid, 1 $lp$	

### For Q.12 to Q.15

Answer the questions given below by appropriately matching the information given in three Column of the following table.

	Column II Column II			Column III		
E.C. of Halogens			Characteristics (I)	Characteristics (II)		
a.	$4s^2 4p^5$	i.	Highest electron gain enthalpy	p.	It is used in the preparation of photosensitive papers, films and plates	
b.	$5s^2 5p^5$	ii.	Highest electronegativity	q.	Pale yellow	
c.	$2s^2 2p^5$	iii.	It does not dissolve in water. It is more soluble in CsI solution than in pure water	r.	Brown red	
d.	$3s^2 3p^5$	iv.	It is obtained from mother liquor obtained from crystallisation of carnalite (called Bittern)	s.	It is used in prepartion of poisnous gases like phosgene, tear and mustard gases.	

- 12. For chlorine, CORRECT combination is:
  - (1) a—iv—r
- (2) d—i—s
- (3) c—ii—q
- (4) d—i—p
- 13. For fluorine, CORRECT combination is:
  - (1) c—ii—q
- (2) c—ii—r
- (3) d—i—s
- (4) d—i—p
- 14. For bromine, CORRECT combination is:
  - (1) a—iv—r
- (2) a—iv—q
- (3) b—iii—p
- (4) b—iii—s
- 15. For iodine, CORRECT combination is:
  - (1) a—iv—r
- (2) a—iv—q
- (3) b—iii—p
- (4) b—iii—s

### Numerical Value Type

- of sodiur
- 1. Sodium iodate is treated with calculated amount of sodium bisulphite to prepare iodine. How many moles of sodium bisulphite are required to prepare one mole of iodine from sodium iodate?
- **2.** In the molecule ICl<sub>3</sub>, how many lone pairs of electrons are associated with iodine?

- 3. In the interhalogen compound  $AB_n$ , what is the maximum value of n?
- **4.** In a given sample of bleaching powder, the percentage of available chlorine is 49. The volume in litres of chlorine obtained if 20 g of the sample is treated with HCl at NTP is.
- 5. What is the oxidation state of iodine in H<sub>5</sub>IO<sub>6</sub>?
- **6.** How many orbitals are involved in the hybridisation of iodine in IF<sub>7</sub>?
- 7. Chlorine water on cooling deposits greenish yellow crystals of formula Cl<sub>2</sub>·XH<sub>2</sub>O. What is the value of X?
- 8. How many lone pairs are associated with I in IF<sub>7</sub>?
- 9. What is the oxidation state of Cl in HClO<sub>4</sub>?
- 10. What is the oxidation state of Cl in HClO<sub>4</sub>?
- 11. For oxyacid HClOx, If x = y = z (x, y and z are natural numbers), then calculate the value of (x + y z) where
  - x = Total number of lone pair on central atom.
  - $y = \text{Total number of } \pi e^{-t}$ 's in the oxyacid.
  - z = Total number of 'O' atoms.
- 12. Covalency of chlorine atom in second excite state is.

# **Archives**

### JEE MAIN

### **Single Correct Answer Type**

- 1. Which of the following exists as covalent crystals in the solid state?
  - (1) Iodine
- (2) Silicon
- (3) Sulphur
- (4) Phosphorus

(JEE Main 2013)

- 2. The correct statement for the molecule CsI<sub>3</sub> is
  - (1) It contains  $Cs^{\oplus}$  and  $I^{\Theta}$  ions
  - (2) It contains  $Cs^{\oplus}$  and  $I^{\Theta}$  and lattice  $I_2$  molecule
  - (3) It is a covalent molecule
  - (4) It contains  $Cs^{\oplus}$  and  $I_3^{\ominus}$  ions

(JEE Main 2014)

- 3. Among the following oxoacids, the correct decreasing order of acid strength is
  - (1) HClO<sub>4</sub> > HClO<sub>3</sub> > HClO<sub>2</sub> > HOCl
  - (2)  $HClO_2 > HClO_4 > HClO_3 > HOCl$
  - $(3) \text{ HOCl} > \text{HClO}_2 > \text{HClO}_3 > \text{HClO}_4$
  - (4)  $HClO_4 > HOCl > HClO_2 > HClO_3$

(JEE Main <sup>2014)</sup>

- 4. Which among the following is the most reactive?
  - (1) Cl<sub>2</sub>

(2) Br<sub>2</sub>

 $(3) I_{2}$ 

(4) ICl

(JEE Main <sup>2015)</sup>

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(JEE Main 2015)

# SE ADVANCED

# <sub>şirgile</sub> Correct Answer Type

- guitagent perioxide in its reaction with KIO4 and NH,OH e se girre si Antropo
  - Reducing agent oxidising agent
  - n Reducing agent, reducing agent
  - 3) (Midising agent, oxidising agent
  - 4) (Iniciting agent reducing agent

### (JEE Advanced 2014)

- which among the following is the most reactive?
  - $(2) B_{T_2}$ (3) I (4) ICI

(JEE Advanced 2015)

### **Multiple Correct Answers Type**

- ). The reagents (s) used for softening the temporary hardness of wher is (are)
  - (I) Ca<sub>7</sub>(PO<sub>4</sub>),
- (2) Ca(OH),
- 3) No.CO.
- (4) NaOC1

(IIT-JEE 2010)

- 2 Which of the following halides react(s) with  $\mathrm{AgNO}_{3(30)}$  to give a precipitate that dissolves in  $\mathrm{Na_2S_2O_{3(ac)}}$ 
  - (1) HCI
- (2) HF
- (3) HBr

(4) HI

[IIT-JEE 2012)

3. For the reaction:

$$\mathsf{I}^{\ominus} - \mathsf{ClO}_{\mathfrak{Z}}^{\ \ominus} - \mathsf{H}_2 \mathsf{SO}_{\mathbf{4}} \longrightarrow \mathsf{CI}^{\ominus} + \mathsf{HSO}_{\mathbf{4}}^{\ \ominus} + \mathsf{I}_2$$

The correct statement(s) in the balanced equation is/are

- (1) Stoichiometric coefficient of HSO, <sup>©</sup> is 6.
- (2) Iodide is oxidised.
- (3) Sulphur is reduced.
- (4) H<sub>2</sub>O is one of the products.

### (JEE Advanced 2014)

- 4. The correct statement(s) regarding, (i) HClO, (ii) HClO<sub>2</sub>,
  - $(\widetilde{\mbox{\scriptsize in}})\,\mbox{HClO}_3$  and  $(\mbox{\scriptsize iv})\,\mbox{HClO}_4,$  is (are)
  - (1) The number of Cl = O bonds in (ii) and (iii) together is
  - (2) The number of lone pairs of electrons on Cl in (ii) and (iii) together is three
  - (3) The hybridization of Cl in (iv) is sp<sup>3</sup>

(4) Amongst (i) to (iv), the strongest acid is (i)

### (JEE Advanced 2015)

- 5. The correct statement(s) about the executions. HClO<sub>4</sub> and HClO, is(are)
  - (1) HClO, is more acidic than HClO because of the resonance stabilization of its anion
  - (2) HClO<sub>4</sub> is formed in the reaction between Cl<sub>2</sub> and H<sub>2</sub>O
  - (3) The central atom in both HClO<sub>2</sub> and HClO is sp<sup>3</sup> hybridized
  - (4) The conjugate base of HClO<sub>2</sub> is weaker base than H<sub>2</sub>O

### (JEE Advanced 2017)

- 6. The colour of the X, molecule of group 17 elements changes gradually from yellow to violet down the group. This due to
  - (1) the physical state of X, at atom temperature changes from gas to solid down the group
  - (2) decrease in HOMO-LUMO gap down the group
  - (3) decrease in  $\pi^* \sigma^*$  gap down the group
  - (4) decrease in ionization energy down the group

(JEE Advanced 2017)

### Linked Comprehension Type

### Paragraph 1

Bleaching powder and bleach solution are produced on a large scale and used in several house hold production. The effectiveness of bleach solution is often measured by iodometry.

- 25 mL of household beach solution was mixed with 30 mL of 0.50 M KI and 10 mL of 4N acetic acid. In the titration of the liberated I<sub>2</sub>, 48 mL of 0.25 N Na<sub>2</sub>S<sub>2</sub>O<sub>2</sub> was used to reach the end point. The molarity of the household bleach solution
  - (1) 0.48 M
- (2) 0.96 M
- (3) 0.24 M
- (4) 0.024 M
- 2. Bleaching powder contains a salt of an oxoacid as one of its components. The anhydride of that oxoacid is
  - (1) Cl<sub>2</sub>O
- (2) Cl<sub>2</sub>O<sub>2</sub>
- (3) ClO<sub>2</sub>
- $(4) Cl_2O_S$

(IIT-JEE 2012)

### Paragraph 2

The reactions of Cl2 gas with cold-dilute and hot-concentrated NaOH in water give sodium salts of two different oxoacids of chlorine, P and Q, respectively. The Cl2 gas reacts with SO2 gas, in presence of charcoal, to give a product R reacts with white phosphorus to give a compound S. On hydrolysis, S gives an oxoacid of phosphorus.

- 3. P and Q, respectively, are the sodium salts of
  - Hypochlorous and chloric acids
  - (2) Hypochlorous and chlorous acids
  - (3) Chloric and perchloric acids
  - (4) Chloric and hypochlorus acids.
- 4. R, S and T, respectively, are
  - (1)  $SO_2Cl_2$ ,  $PCl_5$  and  $H_3PO_4$  (2)  $SO_2Cl_2$ ,  $PCl_3$  and  $H_3PO_3$
  - (3)  $SOCl_2$ ,  $PCl_3$  and  $H_3PO_2$  (4)  $SOCl_2$ ,  $PCl_5$  and  $H_3PO_4$

(JEE Advanced 2013)

### **Matrix Match Type**

This section contains questions each with two columns—I and II. Match the items given in column I with that in column II.

1. The unbalanced chemical reactions given in Column I show missing reagent or condition (?) which are provided in Column II. Match Column I with Column II and select the correct answer using the code given below:

	Column I		Column II
P.	$PbO_2 + H_2SO_4 \xrightarrow{?} PbSO_4 + O_2$ + Other product	1.	NO
Q.	$Na_2S_2O_3 + H_2O \xrightarrow{?} NaHSO_4 +$ other product	2.	I <sub>2</sub>
R.	$N_2H_4 \xrightarrow{?} N_2 + \text{ other product}$	3.	Warm
S.	$XeF_2 \xrightarrow{?} Xe + other product$	4.	Cl <sub>2</sub>

Cod	es:			
	P	Q	R	S
(1)	4	2	3	1
(2)	3	2	1	4
(3)	1	4	2	3
(4)	3	4	2	1

# **Numerical Value Type**

- 1. Based on VSEPR theory, the number of 90 degree F-Br-1 angles in BrF<sub>5</sub> is \_\_\_\_\_\_ (IIT-JEE 2010)
- 2. Reaction of Br<sub>2</sub> with Na<sub>2</sub>CO<sub>3</sub> in aqueous solution give, NaBr and sodium bromate with evolution of CO<sub>2</sub> gas. The number of NaBr molecule involved in the balanced chemical equation is \_\_\_\_\_\_ (IIT-JEE 2011)
- 3. Consider the following list of reagents:

  Acidified  $K_2Cr_2O_7$ , alkaline KMnO<sub>4</sub>, CuSO<sub>4</sub>,  $H_2O_2$ , Cl<sub>2</sub>
  O<sub>3</sub>, HNO<sub>3</sub> and Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>. The total number of reagents that can oxidise aqueous  $I^{\odot}$  ion  $I_2$  is

(JEE Advanced 2014)

# **Answers Key**

### **EXERCISES**

### Single Correct Answer Type

1. (2)	<b>2.</b> (1)	<b>3.</b> (1)	<b>4.</b> (3)	<b>5.</b> (1)
<b>6.</b> (3)	<b>7.</b> (1)	<b>8.</b> (4)	<b>9.</b> (2)	<b>10.</b> (1)
<b>11.</b> (4)	<b>12.</b> (2)	<b>13.</b> (4)	<b>14.</b> (1)	<b>15.</b> (4)
<b>16.</b> (4)	<b>17.</b> (1)	<b>18.</b> (3)	<b>19.</b> (1)	<b>20.</b> (2)
<b>21.</b> (4)	<b>22.</b> (1)	<b>23.</b> (1)	<b>24.</b> (3)	<b>25.</b> (2)
<b>26.</b> (4)	<b>27.</b> (3)	<b>28.</b> (2)	<b>29.</b> (3)	<b>30.</b> (3)
<b>31.</b> (3)	<b>32.</b> (4)	<b>33.</b> (2)	<b>34.</b> (4)	<b>35.</b> (4)
<b>36.</b> (3)	<b>37.</b> (3)	<b>38.</b> (2)	<b>39.</b> (1)	<b>40.</b> (1)
<b>41.</b> (3)	<b>42.</b> (1)	<b>43.</b> (1)	<b>44.</b> (4)	<b>45.</b> (1)
<b>46.</b> (2)	<b>47.</b> (3)	<b>48.</b> (2)	<b>49.</b> (1)	<b>50.</b> (1)
<b>51.</b> (2)	<b>52.</b> (3)	<b>53.</b> (3)	<b>54.</b> (2)	<b>55.</b> (2)
<b>56.</b> (1)	<b>57.</b> (1)	<b>58.</b> (1)	<b>59.</b> (2)	<b>60.</b> (1)
<b>61.</b> (3)	<b>62.</b> (1)	<b>63.</b> (2)	<b>64.</b> (4)	<b>65.</b> (1)
<b>66.</b> (3)	<b>67.</b> (1)	<b>68.</b> (2)	<b>69.</b> (3)	<b>70.</b> (4)
<b>71.</b> (4)	<b>72.</b> (2)	<b>73.</b> (1)	<b>74.</b> (3)	75. (4)
<b>76.</b> (1)	<b>77.</b> (4)	<b>78.</b> (4)	<b>79.</b> (1)	<b>80.</b> (3)
<b>81.</b> (2)	<b>82.</b> (2)	<b>83.</b> (2)	<b>84.</b> (1)	<b>85.</b> (1)
<b>86.</b> (1)	<b>87.</b> (3)	<b>88.</b> (1)	<b>89.</b> (1)	<b>90.</b> (2)
<b>91.</b> (2)	<b>92.</b> (2)	<b>93.</b> (3)	<b>94.</b> (1)	<b>95.</b> (2)
<b>96.</b> (1)	<b>97.</b> (2)	<b>98.</b> (4)	<b>99.</b> (4)	100. (2)
<b>01.</b> (3)	<b>102.</b> (3)	<b>103.</b> (3)	104. (3)	<b>105.</b> (2)
<b>06.</b> (2)	<b>107.</b> (3)	<b>108.</b> (1)	` /	()

### **Multiple Correct Answers Type**

<b>1.</b> (1, 3)	<b>2.</b> (1, 2)	<b>3.</b> (3, 4)
<b>4.</b> (1, 2, 3)	<b>5.</b> (1, 2, 3)	<b>6.</b> (1, 2, 4)

<b>7.</b> (2, 4)	<b>8.</b> (1, 4)	<b>9.</b> (1, 2)
<b>10.</b> (1, 4)	<b>11.</b> (2, 3, 4)	<b>12.</b> (1, 2, 3, 4)
<b>13.</b> (1, 2)	<b>14.</b> (2, 4)	<b>15.</b> (1, 2)
<b>16.</b> (1, 3)	<b>17.</b> (1, 2, 3, 4)	<b>18.</b> (2, 3)
<b>19.</b> (1, 2, 3)	<b>20.</b> (2, 3, 4)	<b>21.</b> (1, 2, 4)
<b>22.</b> (1, 2, 3, 4)	<b>23.</b> (1, 2)	<b>24.</b> (3, 4)
<b>25.</b> (2, 3)	<b>26.</b> (1, 2)	<b>27.</b> (1, 2)
<b>28.</b> (1, 2)	<b>29.</b> (1, 3, 4)	<b>30.</b> (3, 4)
<b>31.</b> (1, 3)	<b>32.</b> (1, 2)	<b>33.</b> (1, 2)
<b>34.</b> (2, 3)	<b>35.</b> (1, 2, 4)	<b>36.</b> (2, 4)
<b>37.</b> (1, 2)	<b>38.</b> (1, 2, 4)	<b>39.</b> (1, 4)
<b>40.</b> (1, 2, 3)	<b>41.</b> (1, 3, 4)	<b>42.</b> (2, 3)
<b>43.</b> (1, 4)	<b>44.</b> (1, 3)	<b>45.</b> (1, 3, 4)
<b>46.</b> (1, 4)	<b>47.</b> (2, 4)	<b>48.</b> (1, 3)

### **Linked Comprehension Type**

		160		
1. (4)	<b>2.</b> (1)	<b>3.</b> (2)	<b>4.</b> (4)	<b>5.</b> (3)
<b>6.</b> (2)	<b>7.</b> (4)	<b>8.</b> (1)	<b>9.</b> (3)	<b>10.</b> (2)
<b>11.</b> (3)	<b>12.</b> (1)	<b>13.</b> (2)	<b>14.</b> (1)	<b>15.</b> (1)
<b>16.</b> (4)	<b>17.</b> (3)	<b>18.</b> (1)	<b>19.</b> (4)	<b>20.</b> (2)
<b>21.</b> (1)	<b>22.</b> (4)	<b>23.</b> (3)	<b>24.</b> (2)	<b>25.</b> (4)

### **26.** (1)

### **Matrix Match Type**

Q.No.	a.	b.	c.	d.
1.	ii	iii, iv	i	iii
2.	ii	i, ii, iii	iv	iv
3.	iii	iv	i	ii

	iii	i	ii	iv
1.	iv	iii	ii	i
5.	iv	i	iii	ii
6.	iii	i	iv	ii
1.	iii	i	ii	iv
8.	iii	ii	iv	i
9.	ii	iii	i	iv
10.	ii–q	iii–p	iv-s	i–r
11.	12 (1)	14 (	1) 15	(3)

12.(2)

6. (7)

11.(2)

**13.** (1)

**14.** (1)

**15.** (3)

# Numerical Value Type

**2.** (2) 1.(5)

7.(8)

**3.** (7) **8.** (0)

**4.** (3) **9.** (7) **5.** (7)

**10.** (7)

12.(5)

### **ARCHIVES**

### **JEE Main**

### **Single Correct Answer Type**

1. (2)

**2.** (4)

**3.** (4)

**4.** (1)

**5.** (2)

### JEE Advanced

**1.**(1)

**2.** (4)

### **Multiple Correct Answers Type**

**1.** (2, 3, 4) **2.** (1, 3, 4) **3.** (1, 2, 4) **4.** (2, 3)

**5.** (1, 3, 4)

**6.** (2, 3)

### **Linked Comprehension Type**

**1.** (3)

**2.** (1)

**3.** (1)

**4.** (1)

### **Matrix Match Type**

**1.** (4)

### **Numerical Value Type**

**1.** (0)

**2.** (5)

**3.** (7)

5

# *p-*Block Group 18 Elements The Inert Family

### **OVERVIEW**

- 1. Group 18 elements comprise helium (He), neon (Ne), argon (Ar), krypton (Kr), xenon (Xe) and radon (Rn).
- Group 18 elements are also known as inert gases, rare gases, noble gases, zerovalent elements or aerogens. However, the names inert gases and rare gases are misnomers.
- 3. General electronic configuration of group 18 elements is  $ns^2 np^6$ , except He, whose electronic configuration is  $1s^2$ .
- 4. Argon is the most abundant noble gas, about 1% by volume in air. It is nearly 30 times more abundant than  $CO_2$  (0.03). In the universe, the order of abundance is He > Ne > Ar > Kr > Xe.
- 5. a. Ionisation enthalpy: He > Ne > Ar > Kr > Xe > Rn
  - b. Melting point: Rn > Xe > Kr > Ar > Ne > He
  - c. Boiling point: Rn > Xe > Kr > Ar > Ne > He
  - d. Ease of liquefaction: Xe > Kr > Ar > Ne > He
- 6. Helium can be diffused through rubber, glass or plastics.
- 7. Noble gases are monoatomic, colourless, odourless, tasteless, sparingly soluble in H<sub>2</sub>O have low melting and boiling points due to weak van der Waals forces of attraction between the noble gas atoms.
- 8. True compounds of He, Ne and Ar are yet not discovered.
- 9. Most of the compounds of noble gases involve only fluorine and oxygen. This is due to the fact that any chemical reactivity shown by noble gases may be attributed to their tendency to lose electrons. For this reason, the combining atoms must be highly electronegative such as F(EN = 4.0) and O(EN = 3.5).
- 10. The only compound of Kr studied in detail is KrF<sub>2</sub>.
- 11. Xe in its compounds exhibits even oxidation states from +2 to +8.

Oxidation state	+2	+4	+6	+8
Compound	XeF <sub>2</sub>	XeF <sub>4</sub>	$XeF_6$	XeO <sub>4</sub>

Xe also shows an oxidation state of +8 in perxenates,  $[XeO_6]^{4-}$ . Perxenates are strong oxidising agent and oxidises  $Cl^{\bigcirc} \longrightarrow Cl_2$ ,  $H_2O \longrightarrow O_2$ ,  $Mn^{2+} \longrightarrow MnO_4^{\bigcirc}$  and  $Ce^{3+} \longrightarrow Ce^{4+}$ .

12. Clathrates: Noble gases form a number of combinations in which gases are trapped into the cavities of crystal

lattices of certain organic and inorganic compounds. These combinations are called cage compounds or clathrate compounds or enclosure. The crystal structure with cavities is called the 'Host' and the atom or molecule entrapped in it is called the 'Guest'. These are non-stoichiometric compounds, e.g., Xe-6H<sub>2</sub>O, quinol clathrate. He and Ne do not form clathrate compounds as the size of the cavity is more than the size of the He or Ne atom.

- 13. Only He forms interstitial compounds with metals.
- Solution of XeF<sub>6</sub> in HF is conducting due to formation of ions.
- 15. Discovery of noble gases:

Helium : Lockyer and Janssen
Neon : Ramsay and Travers

Argon : Lord Rayleigh and Ramsay

Krypton : Ramsay and Travers Xenon : Ramsay and Travers

Radon : Dorn

16. On passing electric discharge through noble gases at low pressure (2 mmHg), the gas starts glowing with a characteristic colour. This phenomenon is used in glow signs also called neon signs. The colour also depends upon the pressure of the gas.

Colour of glow	Noble gas used	Pressure of the gas
Red	Neon	10-18 mm
White	Helium	3–4 mm
Light blue	Argon–Neon mixture + Hg vapours	10–20 mm

The colour can also be modified by the use of coloured glass for the discharged tube.

17. Neon is widely used in neon signs which are used for advertising purposes in the form of brilliant orange-red glow. This colour is changed by mixing argon and mercury vapours with neon to light blue. Since the light of neon signs has better penetrating power through fog and mist so these are used in beacon lights for safety of air navigations.

### 5.2 Inorganic Chemistry

- **18.** Neon lamps are used in botanical gardens and the green houses as these stimulates growth and are effective in the formation of chlorophyll.
- 19. Argon is used for creating inert atmosphere in chemical reactions, welding and metallurgical operations and for filling in incandescent and fluorescent lamps. It is also used in filling Geiger-Counter tubes and thermionic tubes.
- **20.** Krypton-85 clathrate provides a safe and useful source of gauges.

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gauges.

21. Krypton and xenon are also used in gas-filled lamp.
However, these gases are superior to argon but are very
costly. A mixture of krypton and xenon is also used in sone
flash tubes for high speed photography. Radon is used in sone
radioactive research and therapeutics and in the non-surgical
treatment of cancer and other malignant growths.

# GENERAL INTRODUCTION Getomic gases, helium (II)

5. monoatomic gases, helium (He), neon (Ne), argon (Ar), The mollow (Kr), xenon (Xe) and radon (Rn) constitute a separate typic of elements known as **group 18 elements**. known as **group 18 elements**. These elements maily of called as inert gases, rare gases, agree phily of called as inert gases, rare gases, aerogens, noble gases have been called as inert gases, rare gases, aerogens, noble gases pare been zero elements. The names inert gases and rare gases of group zero. Initially these gases were reformed or group gases and rare gases were referred as inert gases me nisnomers. Initially these gases were referred as inert gases ne mission of their chemical inertness. Their inertness was generally hecause to their very stable electronic configurations. With the affillowery of large number of xenon compounds in 1962, it was these gases were also referred. shown the first gases is a glishomer. These gases were also referred as rare gases because of their relatively uncommon existence on earth, but argon constitutes 1,9% by volume of the atmosphere and thus these gases are not

Except Rn, all these gases occur in atmosphere and thus are sometimes referred to as aerogens. Nowadays, they are called noble gases so as to convey the impression that these gases do have some reactivity, just like noble metals such as gold and plainum, which are often reluctant to react and yet are not totally interactive. These elements are also known as zerovalent elements is they show zero valency due to their chemical inertness. Consequently the group to which these elements belong is also known as zero group and these elements are known as group zero elements.

Julius Thomson justified the position of noble gases in the periodic table by giving argument that since there are highly electropositive elements (alkali metals) on extreme left and highly electronegative elements (halogens) on extreme right of the periodic table so there must be a group of elements which should form a bridge between highly electropositive and highly electronegative elements, which should neither be electropositive nor be electronegative, i.e. zero valency, that is why they are also known as group zero elements.

Lord Rayleigh and Sir William Ramsay were awarded the noble prizes in 1904 for their discovery of noble gases.

Element	Sym- bol	Year of discovery	Name of discoverer	Origin of name
Helium	Не	1895	Lockyer and Janssen	From the Greek word, 'helios' which means 'sun'
Neon	Ne	1898	Sir William Ramsay and Travers	From the Greek word, 'neos' which means 'new'
Argon	Ar	1894	Lord Rayleigh and Sir William Ramsay	From the Greek 'argos' which means 'inactive'
Krypton	Kr	1898	Sir William Ramsay and Travers	From the Greek word, 'kryptos' which means 'hidden'.
Xenon	Xe	1898	Sir William Ramsay and Travers	From the Greek word 'xenos' which means 'stranger'
Radon	Rn	1898	Friedrich Ernst Dorn	Named after the element 'radium'. Radon, was called nitron at first from the latin word 'nitens' meaning 'shining'

# 5.2 OCCURRENCE AND ABUNDANCE

On account of their inert nature, noble gases always occur in free state. Radon, being radioactive does not occur in free state as it decays rapidly. Its longest lived isotope has half life of less than four days. The chief sources of noble gases are:

Atmosphere: The total abundance of He, Ne, Ar, Kr and Xe in dry air is about 1% by volume of which Ar is the major component.

ic and physical properties of group 18 elements

able 5.1 Atomic and physical p		Neon	Argon	Krypton	Xenon	Radon*
Property	Helium		Ar	Kr	Xe	Rn
Symbol	Не	Ne		36	54	86
Atomic number	2	10	18		131.30	222.00
Atomic mass (g mol <sup>-1</sup> )	4.00	20.18	39.15	83.80		[Xe] $4f^{14}5d^{10}6s^26p^6$
	$1s^2$	[He] $2s^2 2p^6$	[Ne] $3s^2 3p^6$	[Ar] $3d^{10}4s^26p^6$	[Kr] $4d^{10}5s^25p^6$	[Xe] 4/ 3a 68 6p
Electronic configuration		160	190	200	220	_
Atomic radii (pm)	120		1520	1351	1170	1037
Ionisation enthalpy (kJ mol <sup>-1</sup> )	2372	2080		96	77	68
Electron gain enthalny (kI mol <sup>-1</sup> )	48	116	96	$3.7 \times 10^{-3}$	$5.9 \times 10^{-3}$	$9.7 \times 10^{-3}$
Density (at STP) (g cm <sup>3</sup> -)	$1.8 \times 10^{-4}$	$9.0 \times 10^{-4}$	$1.8 \times 10^{-3}$		161.3	202.0
- onsity (at 511) (g one)		24.6	83.8	115.9		211.0
Melting point (K)	1.2	27.1	87.2	119.7	165.0	
Boiling point (K)	4.2		6.5	9.0	12.6	16.4
Enthalpy of vapourisation	0.09	1.77				
$(1-1 mol^{-1})$	111111111111111111111111111111111111111	10-3	0.934	$1.14 \times 10^{-4}$	$8.7 \times 10^{-6}$	,
Abundance in atmospheric	$5.4 \times 10^{-4}$	$1.8 \times 10^{-3}$	0.934	7.7	92 a	1. The second second
(% volume)	rion thefall i				•	

# 5.3 ATOMIC AND PHYSICAL PROPERTIES

Some of the atomic and physical constants of the noble gases have been summarised in Table 5.1.

### **5.3.1 MONOATOMIC NATURE**

All the 18 group elements are colourless, odourless, monoatomic gases, as all the noble gases have stable  $\rm ns^2np^6$  valence shell electronic configuration, except He whose configuration is  $\rm 1s^2$ . Their monoatomic nature is supported by the following facts :

- 1. The ratio of their specific heat at constant pressure and constant volume, i.e.  $C_p/C_v \approx 1.66$ .
- 2. At STP, 22.4 L of each gas weighs equal to the atomic mass of the gas in grams.

Their monoatomic nature confirms their inert behaviour. They do not form diatomic molecules because they do not possess any unpaired electron. He has the usual property of diffusing through most commonly used laboratory materials such as rubber, glass or plastic.

### 5.3.2 ATOMIC RADII

The atomic radii of the noble gases are the largest in their respective periods. The reason being in case of noble gases the radii is **van der Waals** radii due to instantaneous dipole-induced dipole interaction amongst the noble gas atoms; whereas in other groups it is covalent radii. In case of noble gases, covalent radii cannot be determined as they can be solidified at very low temperature only and at such low temperature X-ray crystallography cannot be performed.

Down the group  $(\downarrow)$ , i.e. from He to Rn, the atomic radii increases primarily because at each successive step new shells are being added and the electron cloud is expanding.

Atomic radii: He < Ne < Ar < Kr < Xe

### 5.3.3 IONISATION ENTHALPY

The ionisation enthalpies of noble gases are the highest as compared to ionisation enthalpies of other members in the same period due to the stable electronic configurations.

Down the group  $(\downarrow)$ , i.e. from the He to Rn, ionisation enthalpy decreases because of increase in atomic radii (size effect) and screening effect of the inner electrons.

Ionisation enthalpy: He > Ne > Ar > Kr > Xe > Rn

### 5.3.4 ELECTRON GAIN ENTHALPY

The electron gain enthalpy of noble gases is positive, as noble gases have completely filled subshells. Hence, the additional electron has to be placed in an orbital of next higher shell. Consequently, energy has to be supplied to add an additional electron and hence, the electron gain enthalpy of noble gases is positive.

Down the group  $(\downarrow)$ , i.e. from He to Rn, as the size of the atom increases, electron gain enthalpies become less positive.

### **5.3.5 MELTING AND BOILING POINTS**

The melting and boiling points of noble gases are extremely low in comparison to those substances of comparable atomic and molecular mass. This is because there is no strong interatomic forces. Only weak **van der Waals** forces operate which hold atoms together in liquid and solid state.

Down the group ( $\downarrow$ ), i.e. their melting and boiling points increase due to increase in the magnitude of van der Wall forces of attraction with the increase in the atomic size. The very are easily vapourised so that they remain gases at the temperature at which most of other elements are liquids or solids.

Helium has the lowest boiling point of any known substance. Gaseous He on cooling below 4.2 K condenses to a liquid known as Helium-I, which on cooling to 2.2 K at 1 atm pressure changes into a remarkable liquid known as Helium-II. Helium-II exhibits the following properties:

- High heat conductance, i.e. 600 times that of Cu at roops
   temperature.
- Low viscosity i.e. 1/1000 th of H<sub>2</sub> gas. Thus it is virtually frictionless.
- It is also able to flow uphill.

### 5.3.6 ENTHALPY OF VAPOURISATION

It gives a measure of energy required to overcome the forces of attraction between noble gas atoms. The forces of attraction between the noble gas atoms are **van der Waals** forces which are very weak and arises due to instantaneous dipole-induced dipole.

Down the group (\$\sqrt{\psi}\$), instantaneous dipole-induced dipole increases or polarisability increases, with increase in atomic size and therefore van der Waals forces increase. Hence enthalpy of vapourisation increases.

Enthalpy of vapourisation: He < Ne < Ar < Kr < Xe < Rn

### 5.3.7 EASE OF LIQUEFACTION

It is relatively difficult to liquefy noble gases due to weak van der Waals forces of attraction between the atoms.

It is only the weak van der Waals forces (London dispersion forces) which are responsible for the liquefaction of these gases.

Down the group  $(\downarrow)$ , with the increase in atomic size, the magnitude of **van der Waals** forces of attraction increases and hence ease of liquefaction increases.

Ease of vapourisation: He < Ne < Ar < Kr < Xe

### 5.3.8 SOLUBILITY IN WATER

Noble gases have relatively high solubility in water, i.e., solubility of Ar in  $H_2O$  is greater than that of  $O_2$  or  $N_2$ .

Down the group (\$\psi\$), i.e. from He to Rn, solubility in walk increases.

Noble gases are soluble in water due to **dipole-induced** dipole **interaction**. Water is a polar molecule. Due to dipole in  $H_2O$ , a induced dipole is created in noble gas atoms, due to distortion or polarisation of otherwise symmetrical electron cloud of noble gas atom (Figure 5.1).

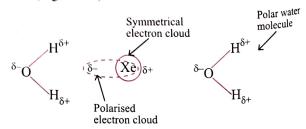


Fig. 5.1 Polarisation of Xe atom by H<sub>2</sub>O molecule

pown the group (\$\dsigma\$), the atomic size increases and the of the electron cloud to its nucleus decreases and his results in greater distortion of their electron cloud by the polarising water molecule. The magnitude of dipole-induced polarite interaction increases with the increasing size of the noble gases and consequently, their solubility in water increases down the group  $(\downarrow)$ .

 $_{Solub}$ ility in water: He  $\leq$  Ne  $\leq$  Ar  $\leq$  Kr  $\leq$  Xe

# 5.4 CLATHRATE COMPOUNDS

Clathrate compounds are also known as cage compounds or inclusion compounds. According to Powell, in the clathrates, atoms or molecules (known as guests) of appropriate size are trapped in the cavities of crystal lattice of other compounds (known as host). Though the gases are trapped, they do not form true chemical bond. The only type of interaction in these compounds is the weak van der Waals forces. Clathrates are normally non-stoichiometric compounds. They are not true chemical compounds.

### Essential conditions for clathrate compounds:

- 1. Presence of cavities of appropriate size in the crystal lattice of the host.
- 2. Size of the guest atom/molecule should be such as to fit in the cavities of the host without bringing any atoms closer together than which corresponds to van der Waals radii of the atom.

### Stability of the clathrate compounds:

Clathrate compounds once formed are extremely stable because:

- 1. The guest molecule/atom fits tightly in the cavities of host molecule.
- 2. The guest molecules within the cages are at minimum potential energy.

Guest molecules can escape the host only when the forces holding the molecular cages together are overcome. This can be achieved by following two methods:

- a. By heating the clathrate compound.
- **b.** By dissolving the clathrate compound in suitable solvent such as alcohol.

### Types of clathrates:

1. Quinol clathrates: When an aqueous solution of quinol

is crystallised under a pressure of 10-40 atm. of Ar, Kr or Xe, the noble gas atoms get trapped in the cavities of  $\sim 4$  Å in the  $\beta\text{-quinol}$  structure. The composition of these clathrates correspond to 3 quinol: 1 noble gas atom, though normally all cavities are not filled.

When the quinol clathrate is heated or dissolved in solvent, the hydrogen bonded arrangement of β-quinol breaks and noble gas escapes.

The smaller noble gases, He and Ne, do not form clathrate compounds because the noble gas atoms are small enough to escape through the cavities.

2. Noble gas hydrates: These are clathrate compounds but more commonly are referred to as noble gas hydrates. The noble gases Ar, Kr and Xe are trapped in the cavities formed when water is frozen under high pressure of gas. Their composition is approximately 6H<sub>2</sub>O: 1 noble gas atom. He and Ne do not form hydrates as they are too small as compared to the size of the cavity and thus escape through the cavities.

### Uses:

- a. Clathrate compounds provide a convenient means of storage and transportation of radioactive isotopes of Kr and Xe produced in nuclear reactors.
- b. Clathrates play an important role in the separation of noble gases. For example, neon can be separated from argon, krypton and xenon by forming clathrates with quinol because neon is the only gas that does not form such clathrates with quinol.
- c. Clathrates play an important role in some physiological actions, e.g., it is thought that the anaesthetic action of xenon is due to aqueous clathrate formation in physiologically strategic spots. When the anaesthetic is no longer administered the clathrates equilibrium is destroyed, the clathrates decompose and the consciousness returns.

## 5.5 INTERSTITIAL COMPOUNDS

Interstitial compounds are formed when small atoms occupy the interstitial space of the metal lattice. Only He forms interstitial compounds since the atomic size of He is the smallest amongst the noble gases and matches the size of the interstices available in the lattice of most of the heavy metals.

# 5.6 CHEMISTRY OF NOBLE GAS COMPOUNDS

The first noble gas compound was made in 1962. Bartlett and Lohman had used highly oxidising compound platinum

hexafluoride, 
$$\operatorname{PtF}_6$$
 to oxidise dioxygen,  $\operatorname{O}_2$ .  

$$\operatorname{PtF}_6 + \operatorname{O}_2 \longrightarrow \operatorname{O}_2^{\oplus} \left[\operatorname{PtF}_6\right]^{\ominus}$$
(red)
Dioxygenyl hexafluoridoplatinate(V)

Since first ionisation enthalpy of 
$$O_2$$
 and  $Xe$  are almost same,
$$O_{2(g)} \longrightarrow O_{2(g)}^{\oplus} + e^{\Theta} \quad 1175 \text{ kJ mol}^{-1}$$

$$Xe_{(g)} \longrightarrow Xe_{(g)}^{\oplus} + e^{\Theta} \quad 1170 \text{ kJ mol}^{-1}$$

it was predicted that Xe should also react with PtF6. It was experimentally shown that when deep red vapours of PtF, were mixed with equal volume of Xe, the gases combined immediately to give yellow solid. It was (incorrectly) thought that the product is  $Xe^{\oplus}[PtF_6]^{\oplus}$  [Xenon hexafluoridoplatinate(V)]. The reaction has since been found to be more complicated, and the product is  $[XeF] \oplus [Pt_2F_{11}]^{\Theta}$ .

PtF<sub>6(g)</sub> + Xe<sub>(g)</sub> 
$$\longrightarrow$$
 Xe <sup>$\oplus$</sup>  [PtF<sub>6</sub>]  $\stackrel{\bigcirc}{\longrightarrow}$  [XeF]  $\stackrel{\bigcirc}{\longrightarrow}$  [XeF]

Soon after this, it was found that Xe and F<sub>2</sub> react at 400°C to give colourless volatile solid XeF<sub>4</sub>. Following this discovery, there was rapid extension of the chemistry of noble gases, in particular of xenon.

- Helium, neon and argon have much higher first ionisation enthalpy as compared to xenon, and hence similar compounds are not formed.
- Ionisation enthalpy of Kr is little lower and it forms KrF<sub>2</sub>.
- Only compounds of radon identified by radiotracer technique is RnF<sub>2</sub>.

Xenon forms stable compounds only with the most electronegative elements, i.e., F (EN = 4.0), O (EN = 3.5) or with highly electronegative groups such as  $OSeF_5$ ,  $OTeF_5$  that contain both oxygen and fluorine.

Of all the noble gases, Xe forms the largest number of compounds. This may be attributed to its low ionisation enthalpy.

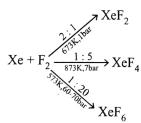
### **5.6.1 FLUORIDES OF XENON**

Xenon reacts directly with fluorine to give binary fluorides:

- 1. Xenon difluoride, XeF,
- 2. Xenon tetrafluoride, XeF<sub>4</sub>
- 3. Xenon hexafluoride, XeF<sub>6</sub>

### Preparation:

 By heating Xe and F<sub>2</sub> at 400°C in a sealed nickel vessel. The products formed depends on Xe: F<sub>2</sub> ratio.



The method is not very good for  $XeF_2$  because it readily reacts further under the experimental conditions to give  $XeF_4$ .  $XeF_6$  can be prepared by the interaction of  $XeF_4$  and  $O_2F_2$  at 143k.

$$XeF_4 + O_2F_2 \longrightarrow XeF_6 + O_2$$

### **Properties:**

1. XeF<sub>2</sub>, XeF<sub>4</sub> and XeF<sub>6</sub> are colourless crystalline solids and sublime readily at 298K. They are powerful fluorinating agents. They are readily hydrolysed even by traces of water.

### 2. Melting point:

Xenon fluoride	$XeF_2$	XeF <sub>4</sub>	XeF <sub>6</sub>
Melting point (°C)	140	117	49.5

Melting point decreases on moving from  $XeF_2$  to  $XeF_4$  to  $XeF_6$ , which is contrary to the usual trend. This is due to increase in polarity as the number of F-atoms bonded to Xe-atom increases.  $F^{\delta+}$ — $Xe^{\delta+}$ — $F^{\delta-}$ . As the number of F-atoms bonded to Xe increases, there is more and more accumulation of +ve charge on Xe, which decreases the stability of the molecule.

Hydrolysis: XeF<sub>2</sub>, XeF<sub>4</sub> and XeF<sub>6</sub>.

(i) 
$$2XeF_2(s) + 2H_2O(l) \longrightarrow 2Xe(g) + 4HF(aq) + O_2(q)$$

(ii) 
$${}^{6}XeF_4 + 12H_2O \longrightarrow {}^{0}4Xe + {}^{+6}2XeO_3 + 24HF + 3O_3$$

(iii) 
$$XeF_6 + 3H_2O \longrightarrow XeO_3 + 6HF$$

Partial hydrolysis of XeF<sub>6</sub>:

(i) 
$$XeF_6 + H_2O \longrightarrow XeOF_4 + 2HF$$

(ii) 
$$XeF_6 + 2H_2O \longrightarrow XeO_2F_2 + 4HF$$

**Note:** Hydrolysis reaction is a non-redox reaction, since the hydrolysis are XeOF<sub>4</sub> and XeO<sub>2</sub>F<sub>4</sub>, where the 0.S. of all elements remain same as it was in reacting state.

3. As fluorinating agent: All xenon fluorides act as strong fluorinating agents.

$$2 \operatorname{XeF}_2 + 2\operatorname{H}_2\operatorname{C} = \operatorname{CH}_2 \longrightarrow \operatorname{FH}_2\operatorname{C} - \operatorname{CH}_2\operatorname{F} + \operatorname{F}_2\operatorname{CHCH}_3 + 2\operatorname{Ne}_2\operatorname{CHCH}_3$$

\_

$$XeF_2 + C_6H_6 \longrightarrow C_6H_5F + Xe + HF$$

XeF<sub>4</sub>:

$$XeF_4 + 2SF_4 \longrightarrow 2SF_6 + Xe$$

$$XeF_4 + Pt \longrightarrow PtF_4 + Xe$$

$$XeF_4 + 2C_6H_6 \longrightarrow 2C_6H_5F + 2HF + Xe$$

XeF<sub>6</sub>:

$$XeF_6 + 8NH_3 \longrightarrow Xe + 6NH_4F + N_2$$

$$XeF_6 + 6HCl \longrightarrow 6HF + Xe + 3Cl$$

4. As an oxidising agent:

XeF,:

Oxidises 
$$Cl^{\Theta} \longrightarrow Cl_2$$
,  $I^{\Theta} \longrightarrow I_2$ , etc.

$$XeF_2 + 2HCl \longrightarrow 2HF + Xe + Cl_2$$

$$XeF_2 + 2KI \longrightarrow 2KF + Xe + I$$

$$XeF_2 + Ce_2^{III} (SO_4)_3 + SO_4^{2-} \longrightarrow 2Ce^{IV} (SO_4)_2 + Xe^{+F_2}$$

XeF<sub>4</sub>:

$$XeF_4 + 2Hg \longrightarrow Xe + 2HgF_2$$

$$XeF_4 + 2KI \longrightarrow 4KF + Xe + 2I_2$$

$$XeF_4 + 4HCl \longrightarrow 4KF + Xe + 2Cl_2$$

XeF.:

$$XeF_6 + 3Hg \longrightarrow Xe + 3HgF_2$$

5. Formation of addition compounds:

XeF<sub>2</sub> acts as fluoride ion donor (Lewis base) and forms complexes with covalent pentafluorides including PF<sub>5</sub>, Asf<sub>5</sub>

SbF<sub>5</sub> and the transition metal fluorides, NbF<sub>5</sub>, TaF<sub>5</sub>, RuF<sub>5</sub>, OsF<sub>5</sub>, RbF<sub>5</sub>, IrF<sub>5</sub> and PtF<sub>5</sub> (Lewis acids). These are thought to have the following structure:

$$\underset{XeF_2 + PF_5}{\text{KeF}_2 + PF_5} \longrightarrow [XeF]^{\oplus} [PF_6]^{\ominus}$$

**XeF**<sub>4</sub> acts as fluoride ion donor (Lewis base) and forms few complexes with PF<sub>5</sub>, AsF<sub>5</sub> and SbF<sub>5</sub>.

$$XeF_4 + SbF_5 \longrightarrow [XeF_3]^{\oplus} [SbF_6]^{\ominus}$$

### [XeF<sub>3</sub>] thas T-shaped structure.

XeF<sub>6</sub> acts both as fluoride ion donor (Lewis base) and as fluoride ion acceptor (Lewis acid).

$$XeF_6 + BF_5 \longrightarrow [XeF_5]^{\oplus} [BF_4]^{\ominus}$$

$$XeF_6 + AsF_5 \longrightarrow XeF_6 \cdot AsF_5$$
 or  $[XeF_5]^{\oplus} [AsF_6]^{\odot}$ 

$$XeF_6 + SbF_5 \longrightarrow [XeF_5]^{\oplus} [SbF_6]^{\ominus}$$

### b. As fluoride ion acceptor

$$XeF_6 + RbF \longrightarrow Rb^{\oplus} [XeF_7]^{\ominus}$$

$$XeF_{\epsilon} + CsF \longrightarrow Cs^{\oplus} [XeF_{7}]^{\ominus}$$

$$XeF_6 + 2NOF \longrightarrow [NO]_2^{\oplus} [XeF_8]^{2-}$$

On heating,  $[XeF_7]^{\odot}$  decomposes as follows:

$$2\text{Cs} \left[\text{XeF}_{7}\right] \xrightarrow{50^{\circ}\text{C}} \text{XeF}_{6} + \text{Cs}_{2} \left[\text{XeF}_{8}\right]^{2-}$$

### 5.6.2 XENON OXIDES

Xenon forms two oxides: (i) xenon trioxide,  $XeO_3$ , and (ii) xenon tetraoxide,  $XeO_4$ .

1. Xenon trioxide, XeO<sub>3</sub>

### Preparation:

By complete hydrolysis of XeF<sub>6</sub> by atmospheric moisture (slow reaction)

$$XeF_6 + 6H_2O \longrightarrow XeO_3 + 6HF$$

### **Properties:**

- a. White hyroscopic and highly explosive solid.
- b. Acts as strong oxidising agent. It oxidises  $Pu^{2^+}$  to  $Pu^{4^+}$  in the presence of  $H^{\oplus}$  ions.

$$3Pu^{2+} + XeO_3 + 6H^{\oplus} \longrightarrow 3Pu^{4+} + Xe + 3H_2O$$

c. Reaction with XeF<sub>6</sub>:

$$XeO_3 + XeF_6 \longrightarrow 3XeOF_4$$

$$3XeOF_4 + XeO_3 \longrightarrow 2XeO_2F_2$$

d.  $XeO_3$  is soluble in water, but does not ionise. In solution, when pH > 10.5 (alkaline medium) it forms hydrogen xenate ion,  $[HXeO_4]^{\odot}$ .

$$(^{+6})$$
 $XeO_3 + NaOH \longrightarrow Na^{\oplus} [HXeO_4]^{\bigcirc}$ 

or 
$$XeO_3 + \overset{\bigcirc}{OH} \longrightarrow [HXeO_4]^{\overset{\bigcirc}{O}}$$
Hydrogen xenate ion

Hydrogen xenate ion,  $[HXeO_4]^{\odot}$  (oxidation state of Xe = +6) disproportionates slowly in solution to give perxenates,  $[XeO_6]^{4-}$  (oxidation state of Xe = +8) and xenon. (oxidation state of Xe = 0)

$$[HXeO_4]^{\ominus} + 2OH \longrightarrow [XeO_6]^{4-} + Xe + O_2 + 2H_2O$$
Percentate ion xenon

Solution of perxentates are yellow and act as powerful oxidising agents.

**e.** With KF or CsF: When a solution of  $XeO_3$  is treated with KF or CsF, an oxo-fluoro salt,  $M^{\oplus}[XeO_3F]^{\ominus}$  is obtained.

$$XeO_3 + KF \longrightarrow K^{\oplus} [XeO_3F]^{\ominus}$$
  
 $CsF + KF \longrightarrow Cs^{\oplus} [XeO_3F]^{\ominus}$ 

f. With XeOF<sub>4</sub>:

$$XeO_3 + XeOF_4 \longrightarrow 2XeO_2F_2$$

2. Xenon tetraoxide, XeO<sub>4</sub>

### Preparation:

By the action of anhydrous or conc.  $H_2SO_4$  on barium perxenate,  $Ba_3[XeO_6]$ .

$$Ba[XeO_6] + 2H_2SO_4 \longrightarrow XeO_4 + 2BaSO_4 + 2H_2O_4$$

### **Properties:**

 $XeO_4$  is not as stable as  $XeO_3$  and decomposes to give Xe and  $O_2$ .

$$XeO_4 \longrightarrow Xe + 2O_2$$

Reaction of perxenate ion [XeO<sub>6</sub>]<sup>4-</sup> with Mn<sup>2+</sup> in acidic medium:

(i) 
$$4H_2O + Mn^{2+} \longrightarrow MnO_4^{\odot} + 5e^- + 8H^{\oplus}$$

(ii) 
$$6H^{\oplus} + 2e^{-} + [XeO_{6}]^{4-} \longrightarrow XeO_{3} + 3H_{2}O_{1}$$

Multiply eq. (i) by 2 and eq. (ii) by 5 and add them. Net equation is:  $(2Mn^{2+} + 14H^{\oplus} + 5[XeO_6]^{4-} \longrightarrow 2MnO_4^{\ominus} + 5XeO_3 + 7H_2O$ 

(iii) Reaction of XeO3 with I<sup>o</sup> ion in acidic medium

(i) 
$$XeO_3 + 9I^{\odot} + 6H^{\oplus} \longrightarrow Xe + 3H_2O + 3I_3^{\odot}$$

(ii) 
$$XeO_3 + 6I^{\odot} + 6H^{\oplus} \longrightarrow Xe + 3H_2O + 3I_2$$

### 5.6.3 XENON OXYFLUORIDES

Xenon forms a number of oxyfluorides such as:

 $XeO_2F_2$  Xenon dioxydifluoride  $XeOF_4$  Xenon oxytetrafluoride  $XeO_3F_2$  Xenon trioxydifluoride  $XeOF_2$  Xenon oxydifluoride

i. Partial hydrolysis of XeF<sub>4</sub> gives XeOF<sub>2</sub>

$$XeF_4 + H_2O \longrightarrow XeOF_2 + 2HF$$

ii. Partial hydrolysis of XeF<sub>6</sub> gives oxyfluorides, XeOF<sub>4</sub> and XeO<sub>2</sub>F<sub>2</sub>.

$$XeF_6 + H_2O \longrightarrow XeOF_4 + 2HF$$
  
 $XeF_6 + 2H_2O \longrightarrow XeO_2F_2 + 4HF$ 

### Properties of XeOF<sub>4</sub>:

**a.** Clear, colourless mobile liquid which can be stored unchanged in Ni containers for long period.

### b. With H<sub>2</sub>:

$$XeOF_4 + 3H_2 \xrightarrow{300^{\circ}C} Xe + H_2O + 4HF$$

$$XeF_4 + SiO_4 \longrightarrow SiF_4 + XeO_3$$

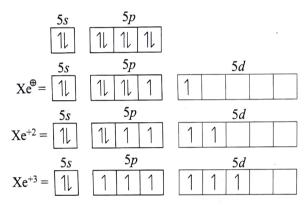
### ILLUSTRATION 5.1

### Explain:

- a. Why does Xe not form fluorides such as XeF, XeF, and
- b. Xe shows +8 O.S. e.g., in XeO<sub>4</sub> but XeF<sub>8</sub> is not formed.
- Neon is used in safety devices for protecting electrical instruments?
- d. Neon is used in warming signal illumination.
- e. Why in deep sea diving a mixture of  $(He + O_2)$  is used rather than  $(Xe + N_2)$  why?

### Sol.

**a.** 
$$Xe = 5s^2 sp^6$$



By unpairing of one period orbitals, two singly occupied orbitals comes into existence. Thus either two, four or six singly occupied orbitals can be formed instead of one, three or five singly occupied orbitals. Hence XeF, XeF3 or XeF5 are not formed.

- b. Eight small sized F atoms can not accomodate one large Eight small sizes sized Xe atom. This is called steric effect or ligand crowding
- c. This is due to the fact that Ne is capable of carrying
- d. This is because Ne light is visible from long distances and mist conditions even visible during fog and mist conditions.
- e. This is due to the fact that at high pressure N<sub>2</sub> gas is highly soluble in blood as compared to He and when the diver comes out of the sea a sudden change in pressure, causes, degassing and releases bubbles of N<sub>2</sub> gas in blood. This causes painful condition called "bends" or caisson sickness He is slightly soluble so risk of bends is reduced

### ILLUSTRATION 5.2

Give the important characteristics of Helium (II).

Sol. Liquid helium is unique in that it exists in two forms He I and He (liquid helium is obtained by Joule-Thomson expansion of the gas previously cooled to 15 K which is below the inversion temperature of He i.e., 35 K). The liquid helium I boils at 4.2 k and has normal liquid properties. On cooling He (I) to 2.19 K and 38 mm pressure, it changes to He (II) with abrupt changes in many physical properties such as density, dielectric constant and specific heat. He (II) is super fluid having so low energy that thermal motion of atoms do not take place, however, interatomic forces are also so weak that it does not occupy solid state. Thus He (II) is liquid with properties of gas. It has following characteristics:

- a. It has very high thermal conductance i.e., 800 times of
- b. It has very low viscosity  $\approx 1/100$  or H<sub>2</sub> gas.
- c. It has a very flat meniscus and very low surface tension and creeps over the surface of glass container.
- d. Its electrical resistance is zero i.e., it is super conducing
- e. He (II) has much lower entropy.

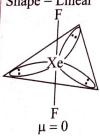
## 5.6.4 VALENCE BOND APPROACH FOR XENON COMPOUNDS

# :XeF,

$$SN = 2 bp + 3 lp = 5$$

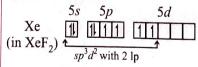
 $H = sp^3d$ , G = Trigonal bipyramidal

Shape = Linear



:XeF4

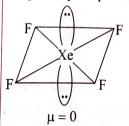
Xenontetrafluoride



$$SN = 4 bp + 2 lp = 6$$

$$H = sp^3d^2$$
,  $G = Octahedral$ 

Shape = Square planar



:XeF<sub>6</sub>

Xenonhexafluoride

$$(in XeF6) \xrightarrow{5s \quad 5p \quad 5d}$$

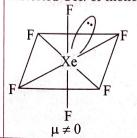
$$sp^3d^3 \text{ with 1 lp}$$

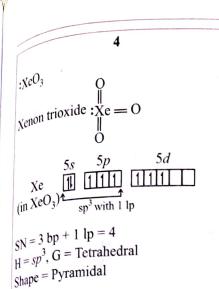
$$SN = 6 bp + 1 lp = 7$$

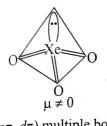
 $H = sp^3d^3$ , G = Pentagonal bipyramidal

Shape = It should be pentagonal pyramid. But it is distorted OH. or monocapped OH.

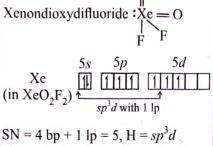
3







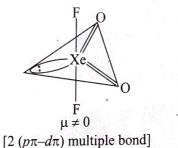
[3  $(p\pi-d\pi)$  multiple bond]



5

:XeO<sub>2</sub>F<sub>2</sub>

 $SN = 4 \text{ bp} + 1 \text{ lp} = 5, H = sp^3 d$  G = T.b.p. See-saw shape saw horse or distorted/irregular. Tetrahedral

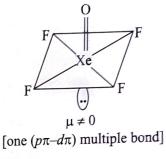


:XeOF<sub>4</sub>

Xenonoxytetrafluoride: Xe = F FXe

(in XeOF<sub>4</sub>)  $Sp^3d^2$  with 1lp

SN = 5 bp + 1 lp = 6,  $H = sp^3d^2$ G = Octahedral, Shape = Square pyramid



XeO<sub>4</sub>: Xenon trioxide

$$\begin{array}{ccc} Xe & 5s & 5p & 5d \\ (\text{in XeO}_4) & & & 11111 \\ & & & & sp^3 \end{array}$$

SN = 4 bp + 0 lp = 4,  $H = sp^3$ , G = Tetrahedral, Shape = Tetrahedral

Note: Electrons used in  $\pi$ -bond formation are not included in the hybridised set of orbitals.

# 5.6.5 VALENCE SHELL ELECTRON PAIR REPULSION (VSEPR) THEORY APPROACH FOR XENON COMPOUNDS

	TALLINGE OF	Structure				
S.No.	Formula	No. of electron	No. of bp	No. of	VSEPR explanation	(shape)
1.	XeF <sub>2</sub> (Xenon difluoride)	$\frac{8+2}{2} = 5$	2	3	5 electron pairs—trigonal bipyramid geometry with 3 lp in equatorial positions	Linear
2.	XeF <sub>4</sub> (Xenon tetrafluoride)	$\frac{8+4}{2}=6$	4	2	6 electron pairs—octahedral geometry, with 2 lp occupying axial position	Square planar  F Xe F

3.	XeF <sub>6</sub> (Xenon hexafluoride)	$\frac{8+6}{2}=7$	6	1	7 electron pairs—pentagonal bipyramidal with 1 lp occupying the axial position OR distorted octahedral	Pentagonal pyramid  F  Xe  F
4.	XeO <sub>3</sub> (Xenon trioxide)	$\frac{8+6}{2}=7$	6	1	7 electron pairs — 3 bp involved in σ bond formation, 3 lp involved in π bond formation and 1 lp. Hence, it forms tetrahedral geometry Shape — pyramidal	Pyramidal  O Xe
5.	XeO <sub>2</sub> F <sub>2</sub> (Xenon dioxy difluoride)	$\frac{8+4+2}{2} = 7$	$\frac{6}{(4\sigma + 2\pi)}$	1	4 bp involved in $\sigma$ bond formation, 2 bp involved in $\pi$ bond formation, 1 lp occupies equatorial position in pentagonal biypramidal geometry	See-saw F
6.	XeO <sub>4</sub> (Xenon tetraoxide)	$\frac{8+8}{2} = 8$	$8 \\ (4\sigma + 4\pi)$	0	4 bp involved in $\sigma$ bond formation, 4 bp involved in $\pi$ bond formation resulting in tetrahedral geometry	Tetrahedral O    Xe O O

Note: Electrons involved in  $\pi$  bond formation must be subtracted before counting the number of electron pairs which determine the primary shape of the molecule.

# 5.7 USES OF NOBLE GASES

# 5.7.1 USES OF HELIUM (He)

- 1. Helium has the lowest boiling point (4.2 K) of any liquid and hence it is used (i) in cryoscopy to obtain the very low temperatures required for superconductivity and lasers; (ii) as a cooling gas in one type of gas cooled nuclear reactor and (iii) as flow gas in gas-liquid chromatography.
- 2. Helium is used in weather balloons and airships. Despite the fact that hydrogen gas has low density, lighter, cheaper and is more readily available than He, it is helium which is used in weather balloons and not hydrogen gas. The reason being that hydrogen gas is highly inflammable as compared to helium. As helium is heavier than H<sub>2</sub>, lifting power of helium is 92.6% as compared to that of H<sub>2</sub>.
- **3.** Due to high thermal conductivity, low viscosity and density, helium is used as flow gas in gas-liquid chromatography.
- **4.** It is used for filling electrical transformers.
- 5. Both helium and nitrogen gas are inert, but it is helium which is used in preference to nitrogen to dilute oxygen in the gas cylinders used by divers in deep sea diving (mixture of (He +  $O_2$ ) is used rather than (He +  $N_2$ ). This is due to the fact that at high pressure,  $N_2$  gas is highly soluble in blood as compared to He and when the diver comes out of the sea, a sudden change in pressure (a region of high pressure to low pressure), causes degassing and releases bubbles of nitrogen

- gas in blood. This causes the painful condition called 'bends' or 'caisson sickness'. Helium is slightly soluble, so the risk of bends is not there or is reduced.
- 6. Helium is used to provide inert atmosphere for the melting of easily oxidisable metals such as magnesium, aluminium. stainless steel etc.
- 7. It is used to produce and sustain powerful conducting magnets, which are essential part of nuclear magnetic resonance (NMR) spectrometer and magnetic resonance imaging (MRI) systems, used for chemical diagnosis.
- 8. Mixture of He and O<sub>2</sub> is used to treat asthma as it is very light and hence diffuses more rapidly than air through partly choked lung passages.
- Helium is suitable for low temperature gas thermomeny because
  - a. It has low boiling point.
  - b. It has near ideal gas behaviour.

## 5.7.2 USES OF NEON (Ne)

- 1. Neon emits a characteristic reddish orange glow when subjected to electric discharge at very low pressure. Hence a small amount of neon is used in neon discharge tubes and fluorescent bulbs for advertising display purposes.
- 2. As the light of neon signs have a better penetrating power through fog and mist so these are used in beacon lights for safety of air navigation.

- 3. Liquid Ne is used as cryogenic refrigerant as it has over 40 times the refrigerating capacity per unit volume than liquid He and three times that of liquid H<sub>2</sub>.
- 4. It is used to make gas lasers.
- 5. Ne bulbs are used in botanical garden and in green houses.

# 5.7.3 USES OF ARGON (Ar)

- 1. Provides inert atmosphere for metallurgical processes. This includes welding stainless steel, titanium, magnesium and aluminium.
- 2. Used in the production of Ti (Kroll's process).
- 3. Mixture of Ar and Hg vapours is used in fluoroscent tubes.
- 4. Argon along with  $N_2$  gas is used in gas-filled electric lamps. It is superior to  $N_2$  gas for filling electric lamps because
  - a. Thermal conductivity is Ar less than that of  $N_2$ .
  - b. At is more inert than  $N_2$  gas, thus it does not endanger the life of the tungsten filament and thereby enhances the life of the lamp.
  - c. Being monoatomic, it does not dissociate even at high temperatures, so no heat is lost in breaking the atoms.
- 5. It is used as a protective (non-reactive) atmosphere for growing crystals of Si and Ge.

## 5.7.4 USES OF KRYPTON (Kr)

- 1. For filling luminous sign tubes and valves.
- 2. Kr-85 is used in electronic tubes for voltage regulation and in leak testers.

## 5.7.5 USES OF XENON (Xe)

- 1. Used in electric flash tubes for high speed photography.
- 2. Xe-133 is used as a radioisotope.
- 3. Perxenates are used in analytical chemistry as oxidising agents.

## 5.7.6 USES OF RADON (Rn)

- 1. Used in radioactive research.
- 2. Used in treatment of cancer and other malignant growths.
- 3. Used for photographing the interiors of opaque materials i.e. locating defects in steel coatings and other metals and solids.

# ILLUSTRATION 5.3

- a. Why are the elements of group 18 known as noble gases?
- b. Noble gases have very low boiling points. Why?
- c. Does the hydrolysis of XeF<sub>6</sub> lead to a redox reaction?

# Sol.

a. The elements present in group 18 have their valence shell orbitals completely filled and therefore react with a few elements only under certain conditions. Therefore, they are known as noble gases.

- **b.** Noble gases being monoatomic have no interatomic forces except weak dispersion forces and therefore, they are liquefied at very low temperatures. Hence they have very low boiling points.
- c. No, the products of hydrolysis are XeOF<sub>4</sub> and XeO<sub>2</sub>F<sub>2</sub>, where the oxidation states of all the elements remain the same as it was in the reacting state.

$$XeF_6 + H_2O \longrightarrow XeOF_4 + 2HF$$
 $(+6)$ 
 $XeF_6 + 2H_2O \longrightarrow XeO_2F_2 + 4HF$ 

## ILLUSTRATION 5.4

- **a.** What prompted Bartlett to the discovery of noble gas compounds?
- **b.** The majority of noble gas compounds are those of xenon. Give reason.
- c. No chemical compound of He is known. Why?

### Sol.

- a. Since PtF<sub>6</sub> oxidises O<sub>2</sub> to O<sub>2</sub><sup>⊕</sup>, Bartlett thought that PtF<sub>6</sub> should also oxidise Xe to Xe<sup>⊕</sup> because the ionisation enthalpies of O<sub>2</sub> (1175 kJ mol<sup>-1</sup>) and Xe (1170 kJ mol<sup>-1</sup>) are quite comparable.
- b. Except Rn, which is radioactive, Xe has the least ionisation enthalpy among group 18 elements and hence can be easily oxidised by strong oxidising agents likes F<sub>2</sub> or O<sub>2</sub>. That is why, majority of noble gas compounds are that of xenon.
- c. Helium does not form chemical compounds because:
  - i. Electronic configuration of He is  $1s^2$ . The unpairing of electron cannot be done in He and hence it cannot form chemical compounds.
  - ii. Ionisation enthalpy of He is very high.

### ILLUSTRATION 5.5

Consider the following compounds in their solid state and find the value of expression. (a + b - c).

$$\mathbf{I.} \ \mathbf{Cl_2O_6} \quad \mathbf{II.} \ \mathbf{I_2Cl_6} \quad \mathbf{III.} \ \mathbf{XeF_6}$$

where  $a = \text{Total number of compounds in which central atom of cationic or anionic part is <math>sp^3$  hybridised.

 $b = \text{Total number of compounds having } 90^{\circ} \text{ bond angle either in cationic or anionic part.}$ 

 $c = \text{Total number of compounds having } 109^{\circ},28' \text{ bond angle either in cationic or anionic part.}$ 

### Sal

I. 
$$\text{Cl}_2\text{O}_6 \Rightarrow [\ddot{\text{C}}\text{IO}_2]^{\oplus} \qquad [\text{CIO}_4]^{\odot}$$
 $sp^2 \qquad sp^3$ 
 $(<120^\circ) \qquad (109^\circ, 28')$ 
 $a = 1, \qquad c = 1.$ 
II.  $\text{I}_2\text{Cl}_6 \Rightarrow [\ddot{\text{I}}\ddot{\text{Cl}}_2]^{\oplus} \qquad [\ddot{\text{I}}\ddot{\text{Cl}}_4]^{\odot}$ 
 $sp^3 \qquad sp^3d^2$ 
 $(<109^\circ, 28') \qquad (90^\circ)$ 
 $a = 1, b = 1$ 
 $c = 1.$ 

III. 
$$\operatorname{XeF}_6 \Rightarrow [\operatorname{XeF}_5]^{\oplus} \operatorname{F}^{\odot}$$
  
 $sp^3 d^2$   
 $(< 90^{\circ})$   
 $b = 1$   
 $\therefore a = 1 + 1 = 2$   
 $b = 1 + 1 = 2$   
 $c = 1 + 1 = 2$   
 $(a + b - c) = (2 + 2 - 2) = 2$ .

### ILLUSTRATION 5.6

Consider the following compounds I to V.

I. XeF.

II. 
$$XeF_{(n+1)}^{\oplus}$$

III. 
$$XeF^{\ominus}_{(n+1)}$$

IV.  $XeF_{(n+2)}$ 

V. 
$$XeF^{-2}_{(n+4)}$$

If the value of n is 4, then calculate the value of (a - b) here, if a = Total number of bond pair on central atom.

b = Total number of lone pair on central atom of compounds I to V.

Sol. (21)

	b.p.	1.p.
I. ∶XeF₄	4	2
II. ∶XeF <sub>5</sub> <sup>⊕</sup>	5	1
III. :ẌeF₅ <sup>⊙</sup>	5	2
IV.:XeF <sub>6</sub>	6	1 .
<b>V.</b> :XeF <sub>8</sub> <sup>2-</sup>	8	1
	28	7
$\therefore (a-b) = (2a-b) = (2a-b)$	(28-7)=21	

# CONCEPT APPLICATION EXERCISE 5.1

- 1. Why helium and neon do not form compounds with fluorine?
- 2. Why neon is used in warning signal illuminations?
- 3. Why helium and neon do not form clathrates with quinol?
- 4. Complete the following reactions:

a.  $XeF_4 + H_2O$ 

**b.**  $XeF_6 + SiO_2$ 

$$\longrightarrow$$

c.  $XeF_2 + H_2$ 

$$\longrightarrow$$

d.  $XeF_6 + H_2O$ 

$$\longrightarrow$$

 $e. XeF_6 + SbF_5$ 

$$\longrightarrow$$

f.  $XeF_6 + NH_3$ 

ordinary conditions?

- 5. Why zero group elements do not form compounds under
- 6. Why Xe does not form fluorides such as XeF, XeF, or XeF5?
- 7. Does the hydrolysis of XeF<sub>6</sub> lead to a redox reaction?

# **Solved Examples**

### EXAMPLE 5.1

XeF<sub>2</sub> has linear structure and not a bent structure. Give reason.

**Sol.** Xe in  $XeF_2$  is  $sp^3d$  hybridised, with 3 lone pairs.

XeF<sub>2</sub> molecule has trigonal bipyramidal geometry. Two of the five  $sp^3d$  orbitals overlap with one 2p orbital of each of the F-atoms to form Xe—F  $\sigma$  bond while the remaining three  $sp^3d$  hybrid orbitals forming the equatorial plane contains lone pair of electrons

To minimise the bp-lp repulsions, Xe—F bonds occupy the axial positions while three lp of electrons occupy equatorial position. Hence, XeF<sub>2</sub> molecule is linear and not bent.



# **Exercises**

# Single Correct Answer Type

# physical and Chemical Properties of Inert Gases

Physical Which of the following does not react with fluorine?

(1) Kr

(2) Ar

(3) Xe

- (4) All of these
- 2. Xenon directly combines with
- (1) oxygen
- (2) rubidium
- (3) fluorine
- (4) chlorine
- 3. Xenon best reacts with
  - (1) the most electropositive element
  - (2) the most electronegative element
  - (3) the hydrogen halides
  - (4) non-metals
- 4. Electron affinity for a noble gas is approximately equal to
  - (1) that of halogens
- (2) zero
- (3) that of oxygen family
- (4) that of nitrogen family
- 5. The gaseous mixture used by deep sea divers for respiration
  - $(1) N_2 + O_2$  mixture
- (2) He +  $O_2$  mixture
- (3) Ar +  $O_2$  mixture
- (4) neon +  $O_2$  mixture
- 6. The forces of cohesion in liquid helium are
  - (1) covalent
- (2) ionic
- (3) van der Waals
- (4) metallic
- 7. The lightest, non-inflammable gas is
  - $(1) H_{2}$

(2) He

 $(3) N_2$ 

- (4) Ar
- 8. The inert gas present in atmosphere are
  - (1) He and Ne
- (2) He, Ne and Ar
- (3) He, Ne, Ar and KR
- (4) He, Ne, Ar, Kr and Xe.
- 9. Inert gases such as helium behave like ideal gases over a wide range of temperature. However, they condense into the solid state at very low temperatures. It indicates that at very low temperature there is a
  - (1) weak attractive force between the atoms
  - (2) weak repulsive force between the atoms
  - (3) strong attractive force between the atoms
  - (4) strong repulsive force between the atoms
- 10. The gas used for inflating the tyres of aeroplanes is
  - $(1) H_2$

(2) He

 $(3) N_{2}$ 

- (4) Ar
- 11. A radioactive element X decays to give two inert gases.
  - $(1) \frac{238}{92} U$

- 12. Which gas is filled in electric bulbs/tubes?
  - $(1) O_{2}$

(2)  $N_2$ 

(3) Ar

- (4) He
- 13. In colour discharge tubes, which is used?
  - (1) Ne

(2) Ar

(3) Kr

- (4) He
- 14. The ease of liquefaction of noble gases decreases in the order

  - (1) He > Ne > Ar > Kr > Xe (2) Xe > Kr > Ar > Ne > He
  - (3) Kr > Xe > He > Ar > Ne (4) Ar > Kr > Xe > He > Ne
- 15. Compounds formed when the noble gases get entrapped in the cavities of crystal lattices of certain organic and inorganic compounds are known as
  - (1) interstitial compounds
- (2) clathrates
- (3) hydrates
- (4) picrates
- 16. Which compound is prepared by the following reaction?

$$Xe + 2F_2 \xrightarrow{\text{Ni vessel}} \frac{\text{Ni vessel}}{673 \text{ K, 5-6 atm}}$$
(1) YeF

(1) XeF<sub>2</sub>

 $(2) XeF_6$ 

 $(3) XeF_4$ 

- (4) XeOF,
- 17. The two electrons in helium atom
  - (1) occupy different shells
  - (2) have different spins
  - (3) have the same spins
  - (4) occupy different subshells of the same subshell
- 18. Helium gives a characteristic spectrum with
  - (1) orange and red lines
- (2) orange lines
- (3) yellow lines
- (4) green lines
- 19. The noble gas which behaves abnormally in liquid state is
  - (1) Xe

(2) Ne

(3) He

- (4) Ar
- 20. In order to prevent the hot metal filament from getting burnt, when the electric current is switched on, the bulb is filled with
  - $(1) CH_{4}$

(2) an inert gas

(3) CO<sub>2</sub>

- (4) Cl<sub>2</sub>
- 21. Radon is a noble gas. Its radioactivity is used in the treatment
  - (1) typhoid
- (2) cancer
- (3) cough and cold
- (4) thyroid
- 22. Helium is used in gas balloons instead of hydrogen because
  - (1) it is higher than H<sub>2</sub>
  - (2) it is non-combustible
  - (3) it is more abundant than  $H_2$
  - (4) its linkage can be detected easily
- 23. A helium atom on losing an electron becomes
  - (1) α-particle

	(2) hydrogen atom		<b>37.</b> \	Which of the fo	ollowing cann	ot be formed?
	(3) positively charged heliu	m ion		$(1) \text{ He}^{2+}$		(2) He <sup>⊕</sup>
	(4) negatively charged heliu			(3) He		(4) He <sub>2</sub>
24.	Liquid flow from a higher	to a lower level. Which of the	38. \	Which stateme	nt regarding F	2
	following liquids can climb	up the wall of the glass vessel in	1	1) It is used in	gas cooled n	iclose man
	which it is placed?		(	2) It is used as	a cryogenic a	gent for carrying out experimen
	(1) Alcohol	(2) Liqiud He	`	at low temp	erature.	out experiment
	(3) Liquid N <sub>2</sub>	(4) Water	(	(3) It is used to	produce and su	ાstain powerful superconducting
25	. Neon is extensively used in			magnets.		an superconducting
	(1) cold storage units		(	(4) It is used to	o fill gas ballo	oons instead of H <sub>2</sub> because it is
	(2) organic compounds					
	(3) medicines	uga lamma	<b>39.</b> 7	The idea that	prompted	Bartlett to prepare first ever
	(4) coloured electric discha		•	compound of h	dere Bases	•0
26		began with the experiments with	(	(1) Low bond (	dissociation ei	nthalpy of F-F in F <sub>2</sub> molecule
	(1) Xe	(2) Kr (4) Ne		(2) High bond		
	(3) Ar		(	(3) Ionisation e	enthalpies of (	2 and Xe are almost same
27	. Which statement about nob	ne gases is not correct?	,	(4) None of the		
	<ul><li>(1) Xe forms XeF<sub>6</sub></li><li>(2) Ar is used in electric bu</li></ul>	lho				as aerogens because
	(3) Kr is obtained during ra		· ·	(1) They occur		
		g point among all the noble gases		(2) They are ra		-
28	In solid argon, the atoms ar					nd in atmosphere
	(1) ionic bonds	(2) hydrogen bonds		(4) None of the		
	(3) van der Waals forces	(4) hydrophobic forces				used by deep sea divers in
29	The van der Waals forces a					en mixture because
	(1) neon	(2) argon				luble in blood than helium
	(3) krypton	(4) xenon				ible in blood than nitrogen
30.	Electronegativity of an iner			(3) Nitrogen is	•	
	(1) high	(2) low				eep under the sea nitrogen and
	(3) negative	(4) zero	42 1			sonous nitric oxide.
31.	, .	onic configuration as of inert gas?				CN <sub>2</sub> gives respectively:
	$(1) Ag^{3+}$	(2) Cu <sup>2+</sup>		$(1) \text{ XeO}_3 \text{ and } (2) \text{ YeO}_3$		(2) XeOF <sub>3</sub> and CaCN <sub>2</sub>
	(3) Pb <sup>4+</sup>	(4) Ti <sup>4+</sup>		$(3) \text{ XeO}_2$ and $(3) \text{ Architecture}$	4	(4) XeOF <sub>2</sub> and CaCO <sub>3</sub>
	Which noble gas is not four					c spectrum with:
	(1) Rn	(2) Kr		(1) Orange and		(2) Yellow lines
	(3) Ne	(4) Ar		(3) Orange line		(4) Green lines
	Which noble gas is more so			which of the compound?	following no	ble gas does not form clathra
	1) He	(2) Ar			(2) V <sub>2</sub>	
	3) Ne	(4) Xe		(-)	(2) Xe	
		ghest and least polarisability			(4) Ar	at the art holium?
	espectively?	gnest and least polarisability				ot true about helium?
	1) He, Xe	(2) Ne, Kr		(1) It can form		bber and plastic material
	3) Kr, Ne	(4) Xe, He				nization energy
,	,	re of for respiration.		(4) It has the l	_	
		•	46	Which compa	owest botting	ed by the following reaction?
	) $O_2$ and $H_2$	(2) O <sub>2</sub> and He	10.			ed by the following rem
	O <sub>2</sub> and Ar	(4) O <sub>2</sub> and Ne		$Xe + F_2$	$\xrightarrow{\text{Ni}} 673 \text{ K}$	
	ne solubility of noble gases		(	(2 : 1) volume	ratio	
` '		(2) He $>$ Ne $>$ Ar $>$ Kr $>$ Xe		(1) XeF <sub>6</sub>		$(2) XeF_2$
(3)	Xe > Kr > Ar > Ne > He	(4) None of the above	(	(3) XeF <sub>4</sub>		(4) None of these

5.14 Inorganic Chemistry

In the clathrates of xenon with water, the nature of bonding water molecule is: between xenon and water molecule is:

(1) Dipole-induced dipole interaction

- (2) Hydrogen bonding
- (3) Coordinate
- (4) Covalent

# Compounds of Inert Gases

18. Which species is not known?

- (1) XeF<sub>6</sub>
- (2) XeF<sub>4</sub>
- (3) XeO<sub>3</sub>
- (4) KrF<sub>6</sub>
- 49. The fluoride which does not exist is
  - (1)  $CF_{\Delta}$

- $(2) SF_{\kappa}$
- (3) HeF<sub>4</sub>
- $(4) \text{ XeF}_{4}$
- 50. The non-existent species is
  - (1) XeF5
- (2) BrF<sub>5</sub>
- (3) SbF<sub>5</sub>
- (4) PF<sub>5</sub>

51. Geometry and hybridisation of Xe in XeOF<sub>4</sub> molecule is

- (1) square planar, sp<sup>3</sup>d<sup>2</sup>
- (2) square pyramidal, sp<sup>3</sup>d<sup>2</sup>
- (3) tetrahedral, sp<sup>3</sup>
- (4) none of the above

52. XeF<sub>4</sub> exists as ..... under ordinary atmospheric conditions.

(1) solid

(2) liquid

(3) gas

(4) none of these

33. The idea which prompted Bartlett to prepare first ever compound of noble gas was

- (1) high bond energy of Xe–F
- (2) low bond energy of F–F in  $F_2$
- (3) ionisation energies of  $O_2$  and xenon were almost similar
- (4) none of the above

54. What are the products formed in the reaction of xenon hexafluoride with silicon dioxide?

- (1)  $XeSiO_4 + HF$
- (2)  $XeF_2 + SiF_4$
- $(3) \text{ XeOF}_{4} + \text{SiF}_{4}$
- (4)  $XeO_3 + SiF_2$

55. XeF<sub>6</sub> on complete hydrolysis gives

- $(1) \text{ XeO}_3$
- (2) XeO
- $(3) \text{ XeO}_2$
- (4) Xe

56. Xenon tetrafluoride has hybridisation and structure as

- (1) sp<sup>3</sup> tetrahedral
- (2) sp<sup>3</sup>d<sup>2</sup> square planar
- (3) sp<sup>3</sup>d<sup>2</sup> pyramidal
- (4) sp<sup>3</sup>d<sup>3</sup> octahedral

57. In the clathrates of xenon with water, the nature of bonding between xenon and water molecule is

- (1) covalent
- (2) hydrogen bonding
- (3) coordinate
- (4) dipole-induced dipole

58. Out of (i) XeO<sub>3</sub> (ii) XeOF<sub>4</sub> and (iii) XeF<sub>6</sub>, the molecules having same number of lone pairs on Xe are

- (1) (i) and (ii) only
- (2) (i) and (iii) only
- (3) (ii) and (iii) only
- (4) (i), (ii) and (iii)

59. Which is planar molecule?

- $(1) XeO_4$
- (2) XeF<sub>4</sub>
- (3) XeOF<sub>4</sub>
- $(4) \text{ XeO}_2 F_2$

- **60.** Which of the following is an explosive compound?
  - (1) XeO<sub>3</sub>
- (2) XeF<sub>2</sub>
- (3) XeOF<sub>2</sub>
- (4)  $XeOF_4$
- 61. Incorrect statement regarding following reactions is:

$$XeF_{6} \xrightarrow{+Excess H_{2}O} 'X' + HF$$

$$+2H_{2}O \xrightarrow{} 'Y' + HF$$

- (1) XeF<sub>6</sub> can undergo partial hydrolysis
- (2) Both are example of non-redox reaction
- (3) 'Y' is an oxyacid of xenon
- (4) 'X' is explosive
- 62. XeF<sub>6</sub> dissolves in anhydrous HF to give a good conducting solution which contains:
  - (1)  $HXeF_6^+$  and  $F^-$  ions
  - (2)  $\mathrm{HF_2}^{\ominus}$  and  $\mathrm{XeF_5}^{\oplus}$  ions
  - (3)  $H^+$  and  $XeF_7^-$  ion
  - (4) None of these
- 63. MF +  $XeF_4 \longrightarrow$  'A' (M<sup>+</sup> = Alkali metal cation)

The state of hybridisation of the central atomin 'A' and shape of the species are:

- $(1) sp^3 d^3$ , distorted octahedral
- (2)  $sp^3d$ , TBP
- (3)  $sp^3d^3$ , pentagonal planar
- (4) No compound formed at all
- **64.** The formation of  $O_2^{\oplus}[PF_6]^{\odot}$  is the basis for the formation of xenon fluorides. This is because:
  - (1) O<sub>2</sub> and Xe have comparable electronegativities
  - (2) O<sub>2</sub> and Xe have comparable ionization energies
  - (3) Both O<sub>2</sub> and Xe are gases
  - (4) O<sub>2</sub> and Xe have comparable sizes
- 65. Consider the following properties of the noble gases.
  - (I) They readily form compounds which are colourless.
  - (II) They readily generally do not form ionic compounds.
  - (III) Xenon has variable oxidation states in its compound.
  - (IV) The smaller He and Ne do not form clathrate compound
  - (1) I, II, III
- (2) II, III, IV
- (3) I, III, IV
- (4) All
- 66. When a solution of XeO<sub>3</sub> is treated with metal fluoride, the product obtained is ......?
  - $(1) M^{\oplus} [XeO_6 F]^{\odot}$
- (2)  $M^{\oplus}$  [XeO<sub>3</sub>F]
- $(3) M^{\oplus} [XeO_2F_2]^{\ominus}$
- (4) None of these
- 67. Xenon tetra-fluoride, XeF<sub>4</sub> is
  - (1) See-saw shape and acts as a fluoride donor with AsF<sub>5</sub>
  - (2) Square planar and acts as fluoride donor with NaF
  - (3) Square planar and acts as a fluoride donor with PF<sub>5</sub>
- (4) Tetrahedral and acts as a fluoride donor with SbF<sub>5</sub> **68.**  $\operatorname{Xe}(g) + \operatorname{PtF}_{6}(g) \longrightarrow A \xrightarrow{\operatorname{PtF}_{6}} B \xrightarrow{\operatorname{PtF}_{6}} C$ 
  - (I)  $Xe^{\oplus}[PtF_6]^{\odot}$

The products are:

- $(II) [XeF]^{\oplus} [PtF_{11}]^{\ominus}$
- $\begin{array}{ll} \text{(I) } Xe^{\oplus} [\text{PtF}_6]^{\odot} & \text{(II) } [XeF]^{\oplus} [\text{PtF}_{11}]^{\odot} \\ \text{(III) } [XeF]^{\oplus} [\text{Pt}_3F_{16}]^{\odot} & \text{(IV) } [XeF_2]^{\oplus} [\text{Pt}_2F_{11}]^{\odot} \\ \end{array}$

5.16 Inorganic Chemistry	
$(V) [XeF3]^{\oplus} [Pt3F16]^{\odot}$	(VI) $[XeF]^{\oplus}$ $[PtF_6]^{\ominus}$
(1) I, VI, II	(2) I, II, III
(3) VI, II, III	(4) I, IV, V
	correctly represents Xe—F bond
length?	concerny represents as
$(1) XeF_4 > XeF_2 > XeF_6$	$(2) XeF_2 > XeF_4 > XeF_6$
(3) $XeF_6 > XeF_4 > XeF_2$	(4) None of these
<b>70.</b> SbF <sub>5</sub> reacts with XeF <sub>4</sub> to f cation and anion in the adduction	form an adduct. The shapes of ct are respectively:
(1) Square pyramidal, octahe	edral
(2) T-shaped, octahedral	
(3) Square planar, trigonal bi	
(4) Square planar, octahedral	
71. Consider the following trans	formations:
(I) $XeF_6 + NaF \longrightarrow Na^{\oplus} [X_6]$	KeF <sub>7</sub> ] <sup>⊖</sup>
(II) $2PCl_5(s) \longrightarrow [PCl_4]^{\oplus} [FCl_4]^{\oplus}$	
<del>-</del> -	$\rightarrow [Al(H_2O)_5OH]^{2+} + H_3O^{\oplus}$
Possible transformations are:	
(1) I, II, III	(2) I, III
(3) I, II	(4) II, III
72. Which of the following is an of XeF <sub>2</sub> and XeF <sub>4</sub> ?	uncommon hydrolysis product
(1) HF	(2) O <sub>2</sub>
(3) Xe	$(4) \text{ XeO}_3$
73. Out of (i) XeO <sub>3</sub> , (ii) XeO <sub>2</sub> F <sub>2</sub> having same number of lone	
(1) (i) and (ii)	(2) (ii) and (iii)
(3) (i) and (iii)	(4) None of these
74. $[HXeO_4]^{\odot} + OH^{\odot} \longrightarrow [X]$	2 2
The products [X] and [Y] in the	
(1) $H_2XeO_4$ and $Xe$	(2) $[XeO_6]^4$ and $XeO_3$
$(3) \text{ XeO}_3 \text{ and Xe}$	(4) $[XeO_6]^{4-}$ and $Xe$
<b>75.</b> $XeF_2$ and $XeF_6$ are separately	
(1) XeF <sub>6</sub> gives O <sub>2</sub> and XeF <sub>2</sub> d	loes not
(2) Neither of them gives HF	
(3) XeF <sub>2</sub> alone gives O <sub>2</sub>	
(4) Both give out $O_2$	
76. Which of the following compositions	ounds has the same number of
lone pairs as in $I_3^{\odot}$	
	(2) XeF <sub>4</sub>
2	(4) XeO <sub>4</sub>
7. The noble gases can be separa	
(1) Adsorption and desorption	
(2) Passing them through suita	
(3) Electrolysis of their fluorid	
(4) Adsorption and desorption	
Which factor is responsible for from He to Xe?	the increase in boiling points

(1) Increase in polarisability (2) Decrease in polarisability

(4) Mono-atomic nature

76

77.

**78.** 

(3) Decrease in I.E.

- **79.** The compound that cannot be formed by  $Xe_{is:}$  $(2) XeF_4$ (1) XeO<sub>2</sub>F<sub>2</sub>(4) XeO<sub>3</sub>  $(3) XeCl_4$ Multiple Correct Answers Type Physical and Chemical Properties
  - 1. The noble gases which do not form any clathrate
    - (1) He

(2) Ne

(3) Ar

- (4) Kr
- 2. Which of the following noble gases do not react  $w_{\parallel h}$ fluorine?
  - (1) Kr

(2) Xe

(3) He

- (4) Ne
- 3. The noble gases found dissolved in some spring water are
  - (1) He

(2) Ne

(3) Kr

- (4) Ar
- 4. Boiling point and melting point of noble gases are in the
  - (1) He < Ne < Ar < Kr < Xe (2) He > Ne >  $K_T > A_T > \chi_e$
  - (3) He < Kr < Ne < Ar < Xe (4) He > Kr > Ne > Ar > Xe
- 5. Which of the noble gases has its ionisation enthalpy close to that of molecular oxygen?
  - (1) Ar

(2) Xe

(3) Kr

- (4) Rn
- 6. The following observations are shown by
  - 1. It is used for filling airships and balloon for meteorological purposes because of it power equal to 92% that of H.
  - 2. With O<sub>2</sub>, it is used by deep sea divers for respiration and also used in the treatment of respiratory diseases like asthma.
  - 3. Providing inert atmosphere in the welding of metals of alloys that are easily oxidised.
  - 4. Used for inflating the tyre of big aeroplanes because of lightness.
  - 5. Used in cryoscopic experiment.
  - (1) Ne

(2) Ar

(3) He

(4) Kr

- 7. He is added to the oxygen supply used by sea divers because (1) it is less soluble in blood than N<sub>2</sub> a high pressure
  - (2) it is lighter than  $N_2$
  - (3) it is readily miscible with  $O_2$
  - (4) it is less poisonous than  $N_2$
- **8.** Which of the following statements are not correct?
  - (1) Ar is no used in electric bulbs.
  - (2) Kr is obtained during radioactive decay
  - (3) Boiling point of helium is the lowest among all noble gases.
  - (4) Xe forms XeOF<sub>4</sub>
- 9. The coloured discharge tubes for advertisement mainly contains

(2) Ne

Vith

(4) Ar

(3) He

- M. Xenon reacts with (1) the most electropositive element
  - (2) the most EN element
  - (3) the hydrogen halide
  - (4) Non-metals
- $K_r > K_r > K_r > N_e > He$ . This order represents
- (1) ease of vapourization
- (2) enthalpy of vapourisation
- (3) ionisation enthalpy
- (4) solubility in water.
- 12. Which of the following statements are true?
- (1) Xenon fluorides are not reactive.
  - (2) Hydrolysis of XeF<sub>6</sub> is a redox reaction.
  - (3) Ionisation enthalpy of molecular oxygen is very close to that of xenon.
  - (4) Only type of interactions between particles of noble gases are due to weak dispersion forces.
- 13. Select the correct order.
  - (1)  $XeF_6 < XeF_4 < XeF_2 (Xe F bond length)$
  - $(2) \text{ XeF}_6 > \text{XeF}_4 > \text{XeF}_2 \text{(melting point)}$
  - (3) He < Ne < Ar < Kr < Xe (boiling point)
  - (4) He > Ar > Kr > Ne > Xe (abundance in air)
- 14. Helium is used as flow gas in gas liquid chromatography due
- (1) high thermal conductivity (2) low density
- (3) low viscosity
- (4) low thermal conductivity

### Compounds of Inert Gases

- 15. XeF<sub>4</sub> on reaction with H<sub>2</sub> gives
  - (1) Xe

(2) HF

 $(3) \text{ XeF}_2$ 

- $(4) \text{ XeF}_6$
- 16. Which of the following compounds cannot be prepared by direct reaction between the constituent elements?
  - (1) XeF

(2) XeO<sub>3</sub>

(3) XeF<sub>4</sub>

- (4)  $XeO_2F_2$
- 17. Which amongst the following statements are correct?
- (1) XeF<sub>4</sub> and SbF<sub>5</sub> combine to form salt.
  - (2) He and Ne do not form clathrates.
  - (3) He has highest boiling point in its group.
- (4) He diffuses through rubber.
- 18. Which of the possible following fluorides of Xenon is impossible?
  - (1) XeF<sub>2</sub>

(2) XeF<sub>4</sub>

 $(3) XeF_6$ 

- $(4) \text{ XeF}_3$
- 19, Xenon fluorides are colourless and at room temperature are:
  - (1) Solid
- (2) Liquid

(3) Gases

- (4) Superfluid
- 20. Discovery of noble gas compounds were the basis of formation of an ionic solid, dioxygenyl hexafluoridoplatinate (V),  $O_2^{\oplus}[PtF_6]^{\odot}$ , when  $O_2$  reacts with  $PtF_6$ . This experiment was carried out by

- (1) Bartlett and Lohman
- (2) Ramsay
- (3) Dawar
- (4) Fischer-Ringe
- 21. Which one of the following does not exist?
  - (1) XeF<sub>2</sub>

(2)  $XeF_4$ 

(3) ArF,

- (4) XeF<sub>6</sub>
- 22. When deep red PtF<sub>6</sub> vapour was mixed with Xe at room temperature to produce a yellow ionic solid. The product is
  - $(1) Xe^{\oplus} [PtF_6]^{\ominus}$
- (2)  $[XeF^{\oplus}] [Pt_2F_{11}]^{\ominus}$
- (3) Both (a) and (b)
- (4) None
- 23. Which of the following reactions of xenon compounds is incorrect?
  - (1)  $XeF_2 + HF \longrightarrow H[XeF_3]$
  - (2)  $XeF_6 + RbF \longrightarrow [XeF_5][RbF_2]$
  - (3)  $XeF_4 + PF_5 \longrightarrow [XeF_3] [PF_6]$

(4) 
$$3XeF_4 + 6H_2O \longrightarrow 2Xe + XeO_3 + 12HF + \frac{1}{2}O_2$$

- 24. Which of the following statements are incorrect?
  - (1) XeOF<sub>4</sub> can be stored in Ni containers for long period.
  - (2) Xenon trioxide on treatment with xenonoxytetra-fluoride
  - (3) Partial hydrolysis of XeF<sub>6</sub> gives oxy-fluorides.
  - (4) When pH > 10.5 xenon trioxide in solution forms hydrogen xenate ion.
- 25.  $XeF_6$  cannot be stored in glass vessel because silica  $(SiO_2)$  in glass reacts with XeF<sub>6</sub> to form
  - $(1) [XeF_5]^{\oplus}$
- $(3) \text{ XeO}_2 \text{F}_2$
- (4)  $XeOF_4$
- 26. Which among the following statements is/are correct?
  - (1) He has lowest boiling point in its group.
  - (2) He diffuses through rubber and polyvinyl chloride.
  - (3) He and Ne do not form clathrate.
  - (4) XeF<sub>4</sub> and SbF<sub>5</sub> combine to form salt.
- 27. Select the correct statement(s) regarding the fluorides of xenon.
  - (1) All three fluorides are volatile, readily subliming at room temperature (298 K).
  - (2) XeF<sub>4</sub> and XeF<sub>6</sub> can act as fluoride ion acceptors as well as fluoride ion donors.
  - (3) All three fluorides are powerful oxidizing agents.
  - (4) All three fluorides are decomposed by water, XeF, slowly and, XeF<sub>4</sub>, and XeF<sub>6</sub> rapidly.
- 28. Select the correct statements.
  - (1)  $XeO_3$  reacts with KI in acidic medium to give  $I_3^{\odot}$  and  $I_5$
  - (2) XeO<sub>3</sub> disproportionate in basic medium
  - (3) Perxenate [XeO<sub>6</sub>]<sup>4-</sup> disproportionate in basic medium.
  - (4) XeF<sub>6</sub> reacts with glass

## Linked Comprehension Type



### Paragraph 1

Noble gases have completely filled valence shell i.e. ns<sup>2</sup>np<sup>6</sup>, except He (1s<sup>2</sup>). Noble gases are monoatomic under normal conditions.

Low boiling points of the lighter noble gases are due to weak van der Waals forces between the atoms and absence of any interatomic interactions. Xe reacts with  $F_2$  to give a series of fluorides namely  $XeF_2$ ,  $XeF_4$ ,  $XeF_6$ .  $XeF_6$  on complete hydrolysis gives  $XeO_3$ .

- 1. Structure of XeF<sub>4</sub> is
  - (1) Linear
- (2) Square planar
- (3) Tetrahedral
- (4) Pyramidal
- 2. Oxidation state of Xe in XeF<sub>2</sub> is
  - (1) + 2

(2) + 4

(3) + 6

- (4) + 8
- 3. Argon is used in arc welding due to its
  - (1) Flammability
  - (2) High calorific value
  - (3) Low reactivity with metal
  - (4) Lower the melting point of metal
- 4. XeF<sub>4</sub> and XeF<sub>6</sub> are expected to be
  - (1) Reducing
- (2) Oxidising
- (3) Inert
- (4) Basic

#### Matrix Match Type

This section contains questions each with two columns—I and II. Match the items given in column I with that in column II.

	Column I (compound)	Column II (hybridisation of Xe)		
a.	XeF <sub>2</sub>	i.	$sp^3d^3$	
b.	XeF <sub>4</sub>	ii.	$sp^3d^2$	
c.	XeF <sub>6</sub>	iii.	$sp^3$	
d.	XeO <sub>3</sub>	iv.	$sp^3d$	
e.	XeO <sub>2</sub> F <sub>2</sub>	v.	$sp^3d^2$	
f.	XeO <sub>2</sub> F <sub>2</sub> XeO <sub>4</sub>	iv.	sp	

	Column I	Column II		
a.	XeF <sub>2</sub>	i.	Square pyramidal	
b.	XeOF <sub>4</sub>	ii.	Linear	
c.	XeF <sub>4</sub>	iii.	Distorted octahedra	
d.	XeF <sub>6</sub>	iv.	Square planar	
e.	XeO <sub>4</sub>	v.	Pyramidal	
f.	XeO <sub>3</sub>	iv.	Tetrahedral	

	Column I		Column II
a.	Neon	i.	Cryogenic
b.	Helium	ii.	Ionisation energy comparable to O <sub>2</sub>
c.	Xenon	iii.	Advertising sign
d.	Argon	iv.	Provides inert atmosphe
e.	Radon	v.	Cancer treatment
f.	Krypton	vi.	High speed photography

#### 4. Match the following:

Compound		Ну	bridisation	Geometry and shap		
a.	XeF <sub>2</sub>	i.	$sp^3$	1.	Linear	
b.	XeF <sub>4</sub>	ii.	$sp^3d^3$	2.	Square planar	
c.	XeF <sub>6</sub>	iii.	$sp^3d^2$	3.	Expected pentagona pyramid but distorte octahedral	
d.	XeO <sub>3</sub>	iv.	$sp^3d^2$	4.	Expected tetrahedral but pyramidal	

#### 5. Match the following:

Co	mpound	Ну	bridisation	Geometry and shape		
a.	XeOF <sub>2</sub>	399	$sp^3d$	1	Expected trigonal but T-shaped	
b.	XeOF <sub>4</sub>	ii.	$sp^3d$	2.	Expected octahedron but square pyramid	
c.	XeO <sub>2</sub> F <sub>2</sub>	iii.	$sp^3d^2$	3.	Trigonal bipyramid with one position occupied	
d.	XeO <sub>3</sub> F <sub>2</sub>	iv.	$sp^3d$	4.	Trigonal bipyramid	
e.	Ba <sub>2</sub> [XeO <sub>6</sub> ] <sup>4-</sup>	vi.	$sp^3d^2$	5.	Octahedron	

	Column I		Column II
a.	XeF <sub>6</sub>	i.	Basic gas evolves on heating
b.	$(NH_4)_2S$	ii.	Oxidising agent
c.	$H_2PO_3^{\Theta}$	iii.	Disproportionation in basic medium/heating
d.	$\mathrm{Cl}_2$	iv.	Reacts with water/hydrolysis
e.	NO <sub>2</sub>		

the items given in Column I with that in Column II and III

, Match	Column I		Column II		Column III
	Reactions		Products		Characteristics
a.	Partial hydrolysis of $XeF_6$ . $XeF_6 + H_2O \longrightarrow \dots + 2HF$	i.	XeF <sub>2</sub>	p.	$sp^3d^2$ , square pyramid
b.	Partial hydrolysis of XeF <sub>6</sub> .  XeF <sub>6</sub> + 2H <sub>2</sub> O → + 4HF	ii.	XeOF <sub>4</sub>	q.	$sp^3d$ , linear
c.	Complete hydrolysis of XeF <sub>6</sub> . XeF <sub>6</sub> + 3H <sub>2</sub> O →+ 6HF	iii.	XeO <sub>2</sub> F <sub>2</sub>	r.	$sp^3d$ , folded square
d.	Complete hydrolysis of $XeF_4$ . $6XeF_4 + 12H_2O \longrightarrow 4Xe + 24HF + 3O_2 + \dots$	iv.	XeO <sub>3</sub>	S.	$sp^3$ , pyramidal.
e.	Xe(in excess) + $F_2(g) \xrightarrow{2:1}$				

For Q. 8 to Q. 11

or the questions given below by appropriately matching the information given in three Column of the following table.

Column I Noble gases		Column II Characteristics (I)		Column III Characteristics (II)
$3s^2 3p^6$	i.	Highest ease of liquefaction	p.	Along with O2, gas is used for deep sea diving
$5s^2 5p^6$	ii.	High thermal conductivity, low viscosity and density.	q.	Forms clathrate compounds
$1s^2$	iii.	Its electronic configuration is: $[He]2s^2 2p^6$	r.	React with PtF <sub>6</sub> to give orange red ionic solid
$2s^2 2p^6$	iv.	Its name is derived from Greak word which means 'inactive'	s.	It is used in discharge tubes and fluorescent bulbs for advertising display purposes

#### & For helium, CORRECT combination is:

- (1) c—ii—p
- (2) c—ii—s
- (3) d—iii—s
- (4) d—iii—p
- 9. For neon, CORRECT combination is:
  - (1) a—iv—q
- (2) a—iv—r
- (3) d—iii—s
- (4) d-i-s
- 10. For argon, CORRECT combination is:
  - (1) a—iv—q
- (2) a—iv—r
- (3) d—iii—s
- (4) d-i-s
- 11. For Xenon, CORRECT combination is:
  - (l) b—i—q
- (2) b-i-q,r
- (3) b—ii—q
- (4) b—ii—q,r

#### Numerical Value Type



- 1. What is the oxidation number of Xe in XeOF<sub>2</sub>?
- 2. What is the total number of electrons present in the last orbit of Argon?
- 3. What is the percentage of Argon in air?
- 4. What is the total number of unpaired electrons in inert gas?
- 5. What is the total number of lone pair of electrons present in Xe in XeF<sub>2</sub>?
- 6. What is the oxidation sate of Xe in XeF<sub>6</sub>?
- 7. How many  $d\pi p\pi$  bonds are there in XeO<sub>4</sub>?

#### **Archives**



## <sup>Single</sup> Correct Answer Type

- 1. The mineral clevite on heating gives (1) He

(2) Xe

(3) Ar

(4) Ra

- 2. Which of the following reactions is an example of redox reaction?

  - (1)  $XeF_4 + O_2F_2 \longrightarrow XeF_6 + O_2$ (2)  $XeF_2 + PF_5 \longrightarrow [XeF]^+ PF_6^-$
  - (3)  $XeF_6 + H_2O \longrightarrow XeOF_4 + 2HF$
  - (4)  $XeF_6 + 2H_2O \longrightarrow XeO_2F_2 + 4HF$

(JEE Main 2017)

- 3. The products obtained when chlorine gas reacts with cold and dilute aqueous NaOH are:
  - (1) ClO and ClO<sub>3</sub>

(2) ClO<sub>2</sub> and ClO<sub>3</sub>

(3) Cl and ClO

(4)  $\mathrm{Cl}^-$  and  $\mathrm{ClO}_2^-$ 

(JEE Main 2017)

#### JEE ADVANCED

#### **Single Correct Answer Type**

- 1. The shape of XeO<sub>2</sub>F<sub>2</sub>, molecule is
  - (1) Trigonal bipyramidal
- (2) Square planar
- (3) Tetrahedral
- (4) See-saw

(HT-JEE 2012)

2. Under ambient conditions, the total number of gases released products in the final step of the reaction scheme shown below

$$XeF_{6} \xrightarrow{Complete \\ Hydrolysis} P + other product$$

$$\downarrow OH^{\Theta}/H_{2}O$$

$$Q$$

$$\downarrow slow disproportionation in OH^{\Theta}/H_{2}O$$

$$Products$$

(1)0

(2) 1

(3)2

(4)3

(JEE Advanced 2014)

- 3. Which one has the highest boiling point?
  - (1) He

(2) Ne

(3) Kr

(4) Xe

(JEE Advanced 2015)

#### Linked Comprehension Type

The noble gases have closed-shell electronic configuration and are monatomic gases under normal conditions. The low boiling points of the lighter noble gases are due to the weak dispersion forces between the atoms and the absence of other interatomic interactions.

The direct reaction of xenon with fluorine leads to a series of compounds with oxidation numbers +2, +4 and +6, XeF<sub>4</sub> reacts violently with water to give XeO<sub>3</sub>. The compounds of xenon exhibit rich stereochemistry and their geometries can be deduced to total number of electron pairs in the valence exhibit rich stereochemes, and the valence shell because of its

- 1. Argon is used in arc welding because of its
  - (1) low reactivity with metals.
  - (2) ability to lower the melting point of metals.
  - (3) flammability
  - (4) high calorific value
- 2. The structure of XeO3 is

(1) linear

(2) planar

(3) pyramidal

(4) T-shaped

3. XeF<sub>4</sub> and XeF<sub>6</sub> are expected to be

(1) oxidising

(2) reducing

(3) unreactive

(4) strongly basic

(IIT-JEE 2007)

#### **Matrix Match Type**

1. All the compounds listed in column I react with water. Match the result of the respective reactions with the appropriate options listed in column II.

	Column I		Column II
a.	(CH <sub>3</sub> ) <sub>2</sub> SiCl <sub>2</sub>	p.	Hydrogen halide formation
b.	XeF <sub>4</sub>	q.	Redox reaction
c.	Cl <sub>2</sub>	r.	Reacts with glass
d.	VCl <sub>5</sub>	S.	Polymerisation
384.3		t.	O <sub>2</sub> formation

(IIT-JEE 2010)

#### Numerical Value Type

1. A list of species having the formula XZ<sub>1</sub> is given below.

 ${\rm XeF_4,\ SF_4,\ SiF_4,\ BF_4^{\ \odot},\ [Cu(NH_3)_4]^{2^+},\ [FeCl_4]^{2^-}.\ [CoCl_4]^{2^+}}$ 

Defining shape on the basis of the location of X and Z atoms the total number of species having a square planar shape s

(JEE Advanced 2014)

2. The total number of lone pairs of electrons in  $N_2O_3$  is

(JEE Advanced 2015)

**75.** (3)

**74.** (4)

**79.** (3)

## **Answers Key**

**71.**(1)

**76.** (1)

**72.** (4)

77. (4)

#### **EXERCISES**

**26.** (4)

#### **Single Correct Answer Type**

**3.** (2) 4. (2) **5.** (2) **2.** (3) 1. (2) 8. (4) **9.** (2) **10.** (2) 7. (4) **6.** (3) 14. (2) **15.** (2) **13.** (2) **12.** (3) **11.** (2) **20.** (2) **19.** (3) **17.** (2) **18.** (3) **16.** (3) **24.** (2) 25. (4) **23.** (3) **22.** (2) **21.** (2) 29. (4) **30.** (4) **28.** (3) **27.** (3)

35. (2) 31. (4) 34. (4) **32.** (1) **33.** (4) 40.(1) **36.** (3) 37. (4) **39.** (3) 38. (4) **45**. (1) 41.(2)**44.** (3) **42**. (1) **43.** (2) **50.** (1) **46.** (2) **49.** (3) **47.** (1) **48.** (4) **55.** (1) 51.(2)**52.** (1) **53.** (3) **54.** (3) 60.(1)**56.** (2) **59.** (2) **57.** (4) **58.** (4) 65.(2)**61.** (3) **64.** (2) **62.** (2) **63.** (3) **70.** (2) 66.(2)**69.** (2) **67.** (3) **68.** (1)

**73.** (1)

**78.** (1)

#### Multiple Correct Answers Type **3.** (1, 4) 1.(1,2)**5.** (2) **6.** (3) 4.(1) **8.** (1, 2) **9.** (2) 7.(1) **11.** (1, 2, 4) **12.** (3, 4) 10.(2) **14.** (1, 2, 3) **15.** (1, 2) 13.(1, 3) **17.** (1, 2, 4) **18.** (4) 16. (2, 4) **21.** (3) **20.** (1) 19.(1) **24.** (2) **23.** (1, 2) 22.(3) **27.** (1, 2, 3, 4) **26.** (1, 2, 3, 4) 25. (2, 3, 4) 28. (1, 4)

## <sub>inked Comprehension Type</sub>

1.(2)

**8.**(1)

**2.**(1)

**9.** (3)

**3.** (3)

**4.** (2)

### <sub>Matrix</sub> Match Type

100				1		•
2 1/0	a	b	c	d	e	f
Q.No.	iv	V	i	iii	iv	iii
1.	ii	i	iv	iii	vi	v
2.	iii	i	ii	iv	vi	v
3.			ii, 3	i, 4		
4.	iv, 1	iii, 2		i, 4	v, 5	
5.	iv, 1	iii, 2	ii, 3		ii, iii, iv	
6.	ii, iv	i, iv	i, iii, iv	ii, iii, iv		
7.	ii, p	iii, r	iv, s	iv, s	i, q	
2 (1)	0	(3)	<b>10.</b> (1)	<b>11.</b> (2)		

**10.** (1)

#### **Numerical Value Type**

1. (4)

**2.** (8)

**4.** (0) **3.** (1)

**5.**(3)

7. (4) **6.** (6)

#### **ARCHIVES**

#### JEE Main

#### Single Correct Answer Type

**1.**(1)

**2.** (1)

**3.** (3)

#### JEE Advanced

#### **Single Correct Answer Type**

1. (4)

**2.** (3)

**3.** (4)

#### **Linked Comprehension Type**

**1.**(1)

**2.** (3)

**3.** (1)

#### **Matrix Match Type**

**1.** (a) p, s (b) p, q

(c) p, q, t (d) p

#### **Numerical Value Type**

**1.** (4)

**2.** (8)

6 d- and f-Block Elements

#### **OVERVIEW**

### ¿Block transition elements (T.E.):

- 1. The *d*-block elements are called transition elements (T.E.). General electronic configuration is  $(n-1) d^{1-10} ns^{1-2}$ .
- 2. Zn. Cd and Hg are called non-typical T.E. They have completely filled (n-1)d orbitals, their atoms are not expected to form covalent bonding amongst themselves, hence they have relatively low melting and boiling points (b. pt.) then the other d-block elements.
- 3. T.E. lie between electropositive (E.P.) s-block elements and electronegative (E.N.) p-block elements in the periodic table.
- 4. In representative elements (*s* and *p* blocks) the valence electrons are present only in the outermost shell while in transition elements, the valence electrons are present in the outermost shell as well as *d*-orbitals of penultimate shell.
- 5. All transition elements are *d*-block elements, but all *d*-block elements are not transition elements.
- 6. The transition elements show both covalent and metallic bonding amongst their atoms..
- The d-block elements do not form ionic compounds so readily as the alkali and alkaline earth metals.
- Unlike the s-block elements, d-block elements have a tendency to form covalent compounds under certain conditions.
- Generally, compounds with lower oxidation state (O.S.) are ionic while the compounds with higher O.S. are covalent.
- 10. All the T.E. have simple ccp, hcp or bcc lattice characteristic of true metals. They have high tensile strength, thermal, electrical conductivity and lustre.
- 11. Melting point (m. pt.) of 3d series rises to maximum and fall as the atomic number (Z) increases except in Mn where m. pt. is minimum. Melting point of T.E. except Zn, Cd and Hg are above 900°C. Mn and Tc (technetiun) have abnormally low m.pt. W (tungsten) has highest melting point (3410°C) amongst T.E.
- 12. In a series, the atomic radii first decrease up to the middle of the series and then become constant and at the end of the series show a slight increase.
- 13. The atomic radii increase down the group (↓) from 3d T.E. series to be 4d T.E. series, but the atomic radii of 4d and 5d T.E. series are almost same, due to the consequence of

- lanthanoid contraction, e.g., size of  $Zr \approx$  size of Hf and size of  $Nb \approx$  size of Ta.
- **14.** Ability to show several O.S. is due to comparable energy of (n-1)d and ns orbitals. Sc, Y, La and Ac do not show variable valency
- 15. Many transition elements exhibit oxidation states which differ from each other only by one unit (e.g., Fe(II) and Fe(III)). This is in marked contrast to the s-block elements which exhibit only the group valency and the p-block elements which exhibit either the maximum group valency or valency less by two units due to inert pair effect.
- 16. In general, the minimum oxidation state shown by any transition element is equal to the number of ns-electrons. For the first five members of each transition series, the highest oxidation state shown, in general, is equal to the sum of ns and (n-1) d-electrons. For the remaining five elements, the maximum oxidation state is not related to their electronic configuration. The highest oxidation state shown by any transition element is +8.
- 17. The + 2 oxidation state becomes more stable while the +3 state becomes less stable from left to right in the periodic table.
- **18.** Some transition elements also show an oxidation state of zero in their compounds e.g., [Ni(CO)<sub>4</sub>] and [Fe(CO)<sub>5</sub>].
- 19. In general, for the first four elements of a transition series, higher oxidation states are more stable than lower oxidation states. For the next five elements lower oxidation states are more stable than higher oxidation state e.g., Cr(III) is more stable than Cr(II) but Mn(II) is more stable than Mn(III).
- 20. IE<sub>2</sub> of the transition series increases almost regularly with increase in atomic number. However the value for Cr and Cu are sufficiently higher than those of their neighbours. This is due to stable configuration of  $\operatorname{Cr}^{\oplus}(3d^5\operatorname{exactly})$  half-filled) and  $\operatorname{Cu}^{\oplus}(3d^{10}\operatorname{completely})$  filled.).
- 21. The 5d-transition elements (Group 4-12) possess higher ionisation energies than 3d and 4d-transition elements due to the greater effective nuclear change (Z<sub>eff</sub>) in 5d-transition elements. This is due to imperfect shielding effect of 4d-electrons in 5d transition elements.
- 22.  $E_{\text{M}^2+/\text{M}}^{\ominus}$  values are more negative than  $E_{2\text{H}^{\oplus}/\text{H}_2}^{\ominus}$  values. (except Cu). These metals (except Cu) evolve  $H_{2(g)}$  and

hence are oxidised easily when reacted with acid solutions.  $E_{\text{Cu}^{2+}/\text{Cu}}^{\Theta}$  is highest (+ 0.34) in first transition series and does not liberate  $H_{2(g)}$  from acids.

- **23.** Cr is unreactive although high negative  $E^{\Theta}_{\text{Cr}^{2+}/\text{Cr}}$  value due to the formation of non-reactive invisible layer of Cr2O3.
- **24.**  $E_{M^{3+}/M^{2+}}^{\Theta}$  of Co and Ni is exceptionally high positive value due to high (negative) hydration enthalpy.
- 25. They show good catalytic properties due to the presence of a number of electrons and their capability to form unstable intermediate compound which readily decomposes yielding product and catalyst.
- 26. Most of the compounds of T.E. are coloured in solid or in aqueous solution. This is due to  $d \in -d\gamma$  or  $t_{2g} - e_g$  transition in the visible range and exhibit complementary colour.
- 27. The T.E. ions having completely filled d-orbitals and completely empty d-orbitals are colourless e.g., Zn<sup>2+</sup>, Cd<sup>2+</sup> and Hg<sup>2+</sup> Cu<sup>⊕</sup>, Ag<sup>⊕</sup> and Sc<sup>3+</sup> and Ti<sup>4+</sup>.
- 28. T.E. and their compounds show paramagnetic behaviour due to the presence of unpaired electron. It is due to spin angular momentum and orbital angular momentum. For 1st T.E. series, the contribution of the orbital angular moment is neglected. Therefore, the magnetic moment is determined by the number of unpaired electrons and is calculated by spin only formula.

$$\mu = \sqrt{n(n+2)}$$
 BM (Bohr magneton)

1 BM = 
$$\frac{eh}{4\pi mc}$$
 = 9.27 × 10<sup>-24</sup> Am<sup>2</sup> or J T<sup>-1</sup>

- 29. T.E. ions have ability to form complexes due to small size. high nuclear charge and a number of vacant d-orbitals of comparable energy.
- 30. They have the ability to form interstitial compounds in which small non-metals occupy the interstitial sites and form bonds with them. These are known as hydrides, carbides, borides, nitrides respectively and hence have high m. pt. than those of pure metals. They are chemically inert, hard and rigid, e.g. steel and cast iron are interstitial compounds of Fe and C. They form nonstoichiometric compounds and have indefinite compositions e.g.,  $Fe_{0.94}O_4$ ,  $TiH_{1.7}$ ,  $VH_{0.56}$

The malleability and ductility of metal decrease and tenacity increases.

- 31. They form alloys due to similarity in their atomic sizes. and the atoms of one element can substitute the atoms of other metals in their crystal lattice. Then m.pt. of alloys are generally high, but the m.pt. of alloys are lower than their pure metals. Alloys of Hg are called amalgams.
- 32. Many transition metal compounds are isomorphous e.g., FeSO<sub>4</sub>·7H<sub>2</sub>O and ZnSO<sub>4</sub>·7H<sub>2</sub>O because of almost equal ionic sizes of these metals.
- 33. Lightest transition metal is Sc (density 3.1 g cm<sup>-3</sup>) and heaviest and densest transition element is Os.
- 34. When the metals like Fe, Co and Ni are placed in magnetic field, their magnetic domains are turned so that all of them point in the same direction giving rise to a large magnetic effect. Such substance are known as ferromagnetic.

- 35.  $Cu^{\oplus}$  with  $d^{10}$  configuration should be stable but  $actual_{\parallel y}$  Cu<sup>2+</sup> ion is more stable than  $Cu^{\oplus}$  ion because of  $increas_{\emptyset Q}$
- **36.** Mn shows maximum state of +7 in KMnO<sub>4</sub>.
- 36. Mn snows management
  37. Highest oxidation state shown by any transition element
  1 coriog and Os in 5d-series)
- 38. Mercury is the only liquid metal at room temperature
- 39. Zinc metal is brittle and hard at room temperature
- 40. Most abundant and most widely used transition metal is iron.
- 41. Mo is used in X-ray tube, Ta in analytic weights and instruments used in surgery of veins.
- 42. TiCl<sub>4</sub> and TiO<sub>2</sub> are used in smoke screens.
- 43. Platinum is inert (or noble metal) but it dissolves in again regia due to the formation of H<sub>2</sub>PtCl<sub>6</sub>.
- 44. Mercurous ions exist as dimer Hg<sub>2</sub><sup>2+</sup> and not as Hg<sup>9</sup> and this explains its diamagnetic nature.
- **45.** The first synthetic element is Tc (Z = 43) (technetium mean artificial).
- **46.** Alnico which is an alloy of Al (12%), Co (50%), Ni (20%), and rest iron is used to make permanent magnets.

#### f-Block elements or inner transition elements or rare earth elements:

#### Lanthanoids

- 1. General electronic configuration:  $(n-2) f(n-1) d^{n-1} n^{-1}$
- 2. f-Block elements are divided into two series:
  - (i) Lanthanoids (Ln) and (ii) Actinoids
- 3. In the electronic configuration of Ln  $(4f^{1-14}, 5d^{0-1})$ electron can shift between f- and d-orbitals depending upon the stability of electronic configuration.
- 4. Lanthanoids having electronic configuration of 4f<sup>2</sup> and  $4f^8$  are not known.
- 5. There is gradual steady decrease in atomic/ionic radii in lanthanoid series from La to Lu and La<sup>3+</sup> to Lu<sup>3+</sup> due 1 lanthanoid contraction.
- 6. Due to lanthanoid contraction, pairs of elements such 15 Zr/Hf, Nb/Ta and Mo/W are almost identical in size. Dut to the same reason, sizes of 5d elements are very similar  $\mathbb{R}$ those of 4d elements and they resemble closely. Thus the separation is difficult. However, they can be separated by ion exchange method using zeolite catalyst and (ii) valend change methods.
- 7. The magnetic moment of f-block elements is calculated by considering spin as well as orbital quantum contribution.

i.e., 
$$\mu_{(S+L)} = \sqrt{4S(S+1) + L(L+1)}$$
 BM

- 8. Sizes of Ln<sup>3+</sup> decrease (from La<sup>3+</sup> to Lu<sup>3+</sup>), the coval<sup>gth</sup> character increases and hence basic strength decreases.
- 9. Their most predominant and stable O.S. is +3, they also exist in +2 and +4 O.S., but they have a tendency to rever back to +3 O.S.
- 10. They show limited number of O.S. because there is a latter energy gap between 4f and 5d subshells.

11. They are used in the production of alloy steel known as mischmetal, which is used in making Mg-based alloy, known as pyrophoric alloys.

- 1. General electronic configuration:  $5 f^{1-14}$ ,  $6d^{0-1} 7s^2$ .
- 2. Actinides having electronic configuration of  $5f^{-1}$ ,  $5f^{-5}$  and 5f<sup>8</sup> are not known.
- 3. Like lanthanoids, there is gradual steady decrease in atomic/ ionic radii in actinoids series from Ac to Lr. This is called actinoid contraction. This contraction is greater from element to element in this series due to poor shielding by 5f-electrons.
- 4. Besides +3 O.S., they show higher state of +4, +5, +6 and +7 also. This is due to very small gap between 5f, 6d and 7s subshell.
- 5. They are more basic, have greater tendency towards complex formation and they are radioactive.

#### Compounds of metals:

#### [ Iron and its compounds

$$Fe(Z=26) \Rightarrow 3d^64s^2$$

It is a reactive metal and do not occur in free state. In combined state it occurs in the form of ores.

#### Some important ores are:

- i. Haematite (Fe<sub>2</sub>O<sub>3</sub>)
- ii. Magnetite (Fe<sub>3</sub>O<sub>4</sub>)
- iii. Limonite (Fe<sub>2</sub>O<sub>3</sub>·3H<sub>2</sub>O) iv. Iron pyrites (FeS<sub>2</sub>)
- v. Copper pyrites (CuFeS<sub>2</sub>)

The following compounds of iron have been discussed in the chapter.

FeSO<sub>4</sub>·7H<sub>2</sub>O (Green vitriol), Fe<sub>2</sub>O<sub>3</sub>, FeO, Fe<sub>3</sub>O<sub>4</sub>, FeS, FeCl<sub>3</sub>, and  $(NH_4)_2SO_4 \cdot FeSO_4 \cdot 6H_2O$ 

#### Some important points of Fe and its compounds:

- 1. Fe<sup>2+</sup> is green and Fe<sup>3+</sup> is yellow.
- 2.  $Fe^{3+}$  is powerful oxidising agent than  $Fe^{2+}$  ion.
- 3. FeCl<sub>3</sub> is used as styptic to stop bleeding from a cut.
- 4. Iron is rendered passive by conc.  $\ensuremath{\mathsf{HNO}}_3$  and other oxidising agents like K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>, KMnO<sub>4</sub>, chloric acid, chromic acid, silver nitrate etc. A specimen of passive iron can be rendered active by scratching the film mechanically or chemically (e.g., immersing in conc. alkali solution, heating in reducing atmosphere of H, or CO).
- 5. Slag is formed only by ferrous oxide (FeO), ferric oxide (Fe<sub>2</sub>O<sub>3</sub>) does not form a slag.
- 6. Iron carbide or cementite is Fe<sub>3</sub>C.
- 7. FeSO<sub>4</sub> is used in manufacture of blue black ink.
- 8. Kipp's base is  $FeS + H_2SO_4$ .
- 9. Mohr's salt is resistant to atmospheric oxidation.
- 10. Copper dissolves in an aqueous solution of FeCl<sub>3</sub>.

### II. Copper (Cu = 29) $\Rightarrow 3d^{10}4s^1$

### Important ores of copper are as follows:

- i. Copper pyrites (chalcopyrite): CuFeS<sub>2</sub> or Cu<sub>2</sub>S·Fe<sub>2</sub>S
- ii. Cuprite (Ruby copper): Cu<sub>2</sub>O

- iii. Copper glance: Cu<sub>2</sub>S
- iv. Malachite: Cu(OH)<sub>2</sub>·CuCO<sub>3</sub>
- v. Azurite: Cu(OH)<sub>2</sub>.2CuCO<sub>3</sub>

The following compounds of Cu have been discussed in the chapter:

CuSO<sub>4</sub>·5H<sub>2</sub>O (Blue vitriol), CuCl<sub>2</sub>·2H<sub>2</sub>O, CuO, Cu<sub>2</sub>O

#### Some important points of Cu and its compounds:

- 1. Copper is the second most useful metal (the first being iron).
- 2. Verdigris is Cu(CH<sub>3</sub>COO)<sub>2</sub>·Cu(OH)<sub>2</sub> i.e., basic copper acetate and is used as a green pigment in paints.
- 3. Matte contains  $Cu_2S + FeS$ .
- 4. Schweitzer's reagent contains copper and is used for dissolving cellulose in the manufacture of artificial silk or
- 5. CuSO<sub>4</sub>·5H<sub>2</sub>O is called blue vitriol or 'Nila thotha'.
- **6.** CuF<sub>2</sub> is an ionic solid.
- 7. CuCl<sub>2</sub> and CuBr<sub>2</sub> are covalent and exist as polymers.
- **8.** CuFeS<sub>2</sub> is called Fool's gold.
- 9. If an arc is struck between the two copper rod dipped in water, a colloidal solution of copper is obtained.
- 10. Cu(NO<sub>3</sub>)<sub>2</sub> is monomeric and Cu<sub>2</sub>(CH<sub>3</sub>COO)<sub>4</sub>·2H<sub>2</sub>O is dimeric in vapour state.
- 11. Blister copper contains 96–98% copper with small amounts of Ag and Au as impurity.
- 12. Bordeaux mixture (CuSO<sub>4</sub> solution + lime) is used as
- 13.  $\text{CuSO}_{4(\text{aq})}$  reacts only with  $I^{\Theta}$  ion but does not react with  $Cl^{\Theta}$ ,  $Br^{\Theta}$  and  $F^{\Theta}$  ions.
- 14. With  $[Fe(CN)_6]^{4-}$ ,  $Cu^{2+}$  gives reddish brown ppt. of  $Cu_2[Fe(CN)_6].$

#### III. Zinc (Zn = 30) $\Rightarrow$ 3 $d^{10}4s^2$

#### Important ores of zinc are as follows:

- i. Zincite (red zinc ore): ZnO
- ii. Franklinite: ZnO·Fe<sub>2</sub>O<sub>3</sub>
- iii. Zinc blende: ZnS
- iv. Calamine (zinc spar): ZnCO<sub>3</sub>

#### Some important points of Zn and its compounds:

- 1. Impure zinc is known as spelter.
- 2. The process of depositing a thin layer of zinc on metals like iron is called Galvanisation. It prevents rusting of iron.
- **3.** Rinman's green, a green pigment is ZnO·CoO.
- 4. Zinc dissolves in alkali forming sodium zincate and hydrogen.

$$Zn + 2NaOH \longrightarrow Na_2ZnO_2 + H_2$$

- 5. Zinc dust is used as a reducing agent.
- **6.** ZnS is used in preparing X-ray screens.
- 7. Zinc sulphide containing trace of radium salt (1 part in 10 million parts) is used as luminous paint for watch dials.
- **8.** Lithopone, a white paint, is  $ZnS + BaSO_4$ .
- **9.** ZnO is called philosopher's wool.

#### IV. Silver Ag $(Z = 47) \Rightarrow 4d^{10}5s^{1}$

Silver is found in the free (native) as well as combined state. Native silver usually occurs and associated with copper and gold.

#### Important ores are as follows:

- i. Argentite (silver glance): Ag<sub>2</sub>S
- ii. Horn silver: AgCl
- iii. Ruby silver (pyrargyrite): 3Ag<sub>2</sub>S·Sb<sub>2</sub>S<sub>3</sub>

Lead and copper ores are generally contaminated with silver. Argentiferous galena (lead sulphide containing argentite as impurity) contains 0.01–0.1% silver.

The following compounds of Ag have been discussed in the chapter:

AgNO<sub>3</sub>(Lunar caustic), AgBr, Ag<sub>2</sub>O, Ag<sub>2</sub>S<sub>2</sub>O<sub>3</sub>.

#### Some important points of Ag and its compounds:

- 1. Silver leaves are used in Ayurvedic and Yunani medicine.
- 2. Molten silver dissolves 20 times its volume of oxygen.
- **3.** Silver amalgam is used in silvering of mirrors and in filling teeth.
- 4. Silver metal is best conductor of heat and electricity.
- 5. Sterling silver (80% Ag, 20% Cu) is used in making Jewellery.
- 6. Silver is not attacked by aqua regia but it reacts with conc.  $H_2SO_4$  and conc.  $HNO_3$ .
- 7. Silver reacts with sulphur or H<sub>2</sub>S forming black Ag<sub>2</sub>S hence silver cutlery is tarnished black by food rich in sulphur (mustard and egg yolk).
- **8. Spitting of silver:** Molten silver absorbs oxygen which is given off on cooling causing violet spurting. This is called spitting of silver.
- **9.** Silvering of mirror is based on reduction of ammonical silver nitrate solution by neutral solution of tartarate or glucose in cold.
- 10. AgNO<sub>3</sub> is called Lunar caustic.
- 11. All silver halides except AgF are insoluble in water.
- 12. AgI is insoluble in  $NH_4OH$  but AgCl is soluble in  $NH_4OH$  due to formation of  $[Ag(NH_3)_2]Cl$ .
- 13. AgBr is most sensitive to photoreduction. AgI is not so sensitive to light. Both AgBr and AgI are used in photography.
- 14. AgO is a brown coloured solid insoluble in water.
- **15.** Silver nitrate is used for preparing marking inks and hair dyes.

#### V. Gold Au (Z = 79) $\Rightarrow 5d^{10}6s^1$

Gold is found in the native (free) as well as in combined state. The following compounds of Au have been discussed in the chapter:  $AuCl_3$  and  $Au_2S$ 

#### Some important ores are as follows:

i. Bismuthaurite: BiAu<sub>2</sub>

ii. Sylvanite (Ag.Au)Te<sub>2</sub> iii. Calverite: AuTe<sub>2</sub>

#### Some important points of Au and its compound:

- Ag, Cu and Au like coinage metals and their reactivity decrease in the order Cu > Ag > Au.
- 2. Gold is soluble in mercury.
- The nobility of metals increases with increase in atomic number from Cu to Au.
- 4. Gold is considered to be the king of metals.
- 5. Fulminating gold: It is  $Au(NH_2) = NH \text{ or } N_2H_3 \cdot Au$ .
- 6. Gold and silver are highly malleable and ductile.
- Purity of gold is expressed in fineness or carat. Pure gold is 24 carats.
- 8. Generally small quantity of other metals like copper are added to gold to make it hard.
- 9. Molten gold has a shining green lustre.
- 10. Purple of Cassius is a colloidal solution of gold.

#### VI. Mercury Hg (Z = 80) $\Rightarrow 5d^{10}6s^2$

#### Important ore is Cinnabar: HgS

The following compounds of Hg have been discussed in the chapter:

Hg<sub>2</sub>Cl<sub>2</sub> (calomel), HgCl<sub>2</sub>) (corrosive sublimate) and HgI<sub>2</sub>.

- 1. Mercuric thiocyanate is used for making Pharaoh's serpents. For this purpose, it is mixed with a little gum made into pellets, which when dried and ignited, yield a serpent like voluminous ash.
- 2. Mercuric salts are more stable than mercurous salts.
- 3. Mercury forms alloys (called Amalgam) with all metals except iron and platinum. Hence, mercury is transported in iron containers.
- 4. When a little of mercury is poured into an AgNO<sub>3</sub> solution, a tree like growth of silver amalgam is produced. This is called **mercury tree**.
- 5. Alkaline solution of K<sub>2</sub>HgI<sub>4</sub> is called **Nessler's reagent** and gives brown precipitate [HgI·HgO·NH<sub>2</sub> or iodide of million's base] with ammonia.
- **6.** Mercuric chloride or **corrosive sublimate** is HgCl<sub>2</sub>. It is poisonous and best antidote for it is white of an egg.
- 7. HgS is used as a cosmetic under the name Vermillion and in Ayurvedic medicine Makardhwaja. HgS produced by either direct combination or by precipitation by H<sub>2</sub>S is black in colour. This black HgS on sublimation gives the bright red coloured product used as vermillion or as Makardhwaja.
- 8. Mercury vapour is invisible and has no shining appearance as the liquid metal has.
- 9. Calomel, Hg<sub>2</sub>Cl<sub>2</sub> is used for making standard calomel electrode, used as a reference electrode.
- 10. Mercury is the liquid metal at room temperature.

6.1 INTRODUCTION b. I relements are elements of d-block and consist of elements  $f^{\text{polition}}$  and p-blocks starting from  $f^{\text{political}}$ The periodic table contains s and The d-block of the periodic table contains the elements of the The  $\frac{a}{3-12}$  in which d-orbitals are progressively filled in each good four long periods. In these elements  $\frac{a}{3}$ four long periods. In these elements the differentiating of the life the last electron) enters the popular of the road (i.e. the last electron) enters the penultimate subshell i.e. electron (i.e. the last electron)

 $\binom{n-1}{d}$  subshell. The general electronic configuration of these metals is The  $\frac{1}{n} = \frac{1}{n} =$  $(n-1)^n$  those of s and p-block elements. All these elements are transitional between those of s and p-block elements.

Strictly speaking, a transition element is defined as one which but the state of the state of  $\frac{1}{2}$  but the

its stable oxidation state (O.S.). Thus, Zn, Cd and Hg of group 12 having full  $d^{10}$  configuration in their ground state as well as in their common oxidation states (e.g.,  $Zn^{2+}$ ,  $Cd^{2+}$  and  $Hg^{2+}$ ) are not regarded as transition metals. However, being the end members of three transition series, their chemistry is studied along with the chemistry of the transition metals.

In modern terminology, the general electronic configuration of transition metals is  $(n-1) d^{1-9} ns^{1-2}$ .

Fe, Cu, Ag and Au are among the transition elements that have played important roles in the development of human civilisation.

The elements constituting the f-block are those in which 4f and 5f-orbitals are progressively filled in the latter two long periods; these elements are formal members of group 3 from which they have taken out to form a separate f-block of the period table. The name inner transition metals are often used to refer to the elements of f-block elements.

The inner transition elements such as Th, Pa and U are excellent sources of nuclear energy in modern times.

Table 6.1 Outer electronic configurations of the transition elements (ground state)

o- III B	IV B 4	V B 5	VI B	VII B 7	VIII B 8	VIII B	VIII B 10	1 B 11	II B 12
				1st or 3d	Series				00
21 SC Scandium	22 <b>Ti</b> Titanium	23 <b>V</b> Vanadium	Cr	25 Mn Manganese	Fe	CO Cobalt	Ni Nickel	Cu Copper	Zn Zinc
	2	2		2	2	2	2	1	2
1	2	3	5	5	6	7	8	10	10
1				2nd or 4d	/ Saries				
39 <b>Y</b>	40 Zr	Nb	42 Mo Molybdenum	43 TC	44 Ru	Rh	46 Pd Palladium	Ag Silver	Cd Cadmium
Yttrium	Zirconium	Niobium 1	Molybaenum 1	1	1	1	0	1	2
2	2		5	6	7	8	10	10	10
1	2	4	3	Service of the service of	/ Carios				
La	72 <b>Hf</b>	73 <b>Ta</b>	74 W Tungsten	3rd or 50 75 Re	76 Os Osmium	77 <b>Ir</b> Iridium	Pt Platinum	79 Au Gold	Hg Mercury
Lanthanum 2		Tantalum 2	2	2	2	2	1	1	by Di
	2	3	4	5	6	7	9	10	10
1 1	2			4th or 6c	Series		*	1.5	442
89 Ac	104 <b>Rf</b>	105 Db	106 Sg <sub>Seaborgium</sub>	107 <b>Bh</b>	108	109 Mt Meitnerlum	DS Darmstadtium	Roentgentium	Cn Copernicu
Actinium	Rutherfordium	3 15 C22 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1	2	2	2	2	2	1	10
s 2	2	3	4	5	6	7	8	, 10	1,000

## 6.2 CLASSIFICATION OF d-BLOCK ELEMENTS

These are divided into four transition series:

<sup>1.</sup> The first transition series (3d-series) involves the filling of 3d-orbitals and has 10 elements from scandium (Z=21) to zinc (Z=30) in the fourth period.

- **2. The second transition series** (4d-series) involves the filling of 4d-orbitals and has 10 elements from ytterium (Z = 39) to cadmium (Z = 48) in the fifth period.
- 3. The third transition series (5*d*-series) involves the filling of 5*d*-orbitals and has 10 elements. The first element of this series is lanthanium (Z = 57). It is followed by 14 elements (lanthanides or lanthanons involving filling of 4*f*-orbitals). The next nine elements are from hafnium (Z = 72) to mercury (Z = 80).
- **4. The fourth transition series** (6d-series) involves the filling of 6d-orbitals and is incomplete starting from actinium (Z = 89) and extend up to element with atomic number 104.

## 6.3 ELECTRONIC CONFIGURATION OF d-BLOCK ELEMENTS

- 1. Electronic configuration of *d*-block elements: The general electronic configuration of these elements are  $(n-1)^{1-10} ns^{1-2}$ . The (n-1) stands for inner (i.e. penultimate) *d*-orbitals, have 1–10 electrons and outermost *ns* orbitals have 1–2 electrons.
- 2. In the representative elements (*s* and *p*-block elements), the valence electrons are present only in the outermost shell while in the transition elements, the valence electrons are present in the outermost shell as well as in the inner *d*-orbitals i.e., penultimate shell.
- 3. Due to very little difference in the energies of (n-1)d and ns orbitals, the electrons from both these orbitals may be involved in bond formation.

## 6.3.1 EXCEPTIONAL ELECTRONIC CONFIGURATION IN 3d SERIES

In 3d transition elements, the exceptions are observed in the electronic configuration of Cr (Z = 24) and Cu (Z = 29).

- 1. Expected electronic configuration of Cr (Z = 24) and Cu (Z = 29) are [Ar]  $3d^44s^2$  and [Ar]  $3d^94s^2$  respectively.
- 2. The observed electronic configuration of Cr and Cu are, [Ar]  $3d^54s^1$  and [Ar]  $3d^{10}4s^1$  respectively.

**Explanation:** The energy gap between the two sets (3d and 4s) of orbitals is small enough to prevent electron entering the 3d orbitals to attain additional stability by the atom by either having half-filled configuration  $(d^5)$  or completely filled configuration  $(d^{10})$ . The extra stability of half-filled or fully filled configuration can be explained on the basis of **exchange energy** and **symmetrical distribution of electrons**.

## 6.3.2 EXCEPTIONAL ELECTRONIC CONFIGURATION IN 4d AND 5d TRANSITION ELEMENTS

In 4d and 5d series, the valence electronic configuration of Mo  $(Z = 42)(4d^55s^1)$ , Pd (Z = 46)  $(4d^{10}5s^0)$ , Ag (Z = 47)  $(4d^{10}5s^1)$ ,

Pt (Z=78)  $(5d^96s^1)$  and Au (Z=79)  $(5d^{10}6s^1)$  are explained on the basis of the concept that half-filled and completely filled d-orbitals are relatively more stable than the other d-orbitals.

On the basis of the above concept it is, however, not easy to explain the irregularities found in the observed electronic configurations of the atoms of other elements, since one has to consider the net effect of so many other factors such as (i) nuclear attraction, (ii) shielding of one electron by several other electrons, (iii) inter-electronic repulsion, (iv) the exchange energy forces etc. All these factors play an important part together in determining the final stability of an electronic configuration of an atom.

The properties of transition elements of any given period are not so much different from one another as those of the same period of non-transition elements. The reason of this fact lies in the electronic configuration of transition elements. The electronic configuration of transition elements is invariably  $(n-1)d^{10}ns^{1-2}$  which indicates that (i) the electronic configurations of transition elements differ from one another only in the number of electrons in d orbitals in the (n-1) th shell and (ii) the number of electrons in the outermost shell, ns, is invariably 1 or 2.

## 6.3.3 Zn, Cd and Hg Not Regarded as Transition Elements

Strictly speaking, transition elements are those elements which have incompletely filled (n-1) d-orbitals in its ground state or any one of its oxidation state.

The valence electronic configuration of Zn, Cd, Hg and their ions (e.g.  $Zn^{2+}$ ,  $Cd^{2+}$  and  $Hg^{2+}$ ) are as follows:

$$Zn (Z = 30)$$
:  $3d^{10}4s^2$ ,  $Zn^{2+} = 3d^{10}$   
 $Cd (Z = 48)$ :  $4d^{10}5s^2$ ,  $Cd^{2+} = 4d^{10}$   
 $Hg (Z = 80)$ :  $5d^{10}6s^2$ ,  $Hg^{2+} = 5d^{10}$ 

The (n-1) d-orbitals in these elements and their dipositive ions are completely filled, therefore they are not regarded is transition elements. They do not show properties of transition elements to any appreciable extent except for their stability to form complexes. However, being the end elements of three transition series, they are generally studied with the d-block elements.

## 6.3.4 Cu, Ag and Au REGARDED AS TRANSITION ELEMENTS

Although the (n-1) d-orbitals in these elements are completely filled, yet they are considered as transition elements. This is  $du^{e/l}$  the fact that (n-1) d-orbitals of these elements in their completely oxidation states are incompletely filled. For example,

Element	Valence E.C.	Less stable O.S.	More stable
Cu $(Z = 29)$	$3d^{10}4s^1$	Cu <sup>⊕</sup> : 3d <sup>10</sup>	Cu <sup>24</sup> : 3d
Ag(Z=47)	$4d^{10}5s^1$	$Ag^{\oplus}$ : $4d^{10}$	$Ag^{2}:40$
Au (Z = 79)	$5d^{10}6s^1$	$\mathrm{Au}^{\oplus}$ : $5d^{10}$	Au

Obviously, Cu and Cu<sup>®</sup> (cupric ion), Ag and Ag ion and Au ions cannot be considered as transition elements

they do not exhibit the characteristic properties of why they do not exhibit the characteristic properties of transition elements.

Forbitals, and hence these elements However can and hence these elements are regarded as manufition elements.

## ILLUSTRATION 6.1

On what ground can you say that scandium (Z=21) is a transition of the second but zinc (Z = 30) is not?

On the basis of incompletely filled 3d orbitals in case scandium atom in its ground state (3d<sup>1</sup>), it is regarded as a of scanner element. On the other hand, zinc atom has completely in the ground sate as well as in its oxidised hence it is not regarded as a transition element.

### 6.4 GENERAL CHARACTERISTICS OF TRANSITION ELEMENTS

- 1. The d-orbitals are more influenced by the surrounding and also affect the atom or molecule surrounding them, because d-orbitals of the transition elements project to the periphery of an atom more than s and p-orbitals. Hence, the d-electrons affect the properties of elements to a great extent. Thus ions with similar  $d^n$  configuration (n = 1 - 9) have similar magnetic and electronic properties.
- 2. There are greater horizontal similarities in the properties of the transition elements in contrast to main group elements. However, some group similarities also exist.
- 3. All transition elements show typical metallic properties such as malleability and ductility, high tensile strength, high thermal and electrical conductivity and metallic lustre.
- 4. With the exception of Zn, Cd, Hg and Mn they have one or more typical metallic (lattice) structure at normal temperatures, as shown in Table 6.2.

Table 6.2 Lattice structures of transition metals

	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
;)	hcp	bcc	bcc (bcc,	X	bcc (hcp)	сср	сср	сср	X (hcp)
	Zr	Nb	ccp)	Tc	Ru	Rh	Pd	Ag	Cd
	hen	bcc	bcc	hcp	hcp	сср	сср	сср	X (hcp)
	Hf	Ta	· W	Re	Os	Ir	Pt	Au	Hg
	hcp (bcc)	bcc	bcc	hcp	hcp	сср	сср	сср	X

Note: (bcc = body centred cubic; hcp = hexagonal close packed; ccp = cubic close packed; X = a typical metal structure)

- 5. Their atomic radii are in-between those of s and p-block elements. In a series, they decrease with increase in atomic number but the decrease is small after midway.
- 6. They have high melting and boiling points, high enthalpies of vaporisation, high enthalpies of atomisation and high

- enthalpies of hydration of their ions. These properties depend upon the strength of the metallic bond in them.
- 7. Their first ionisation energies are higher than those of s-block elements and less than those of p -block elements.
- **8.** They show variable oxidation states.
- 9. The stability of any oxidation state or the tendency for a transition metal ion to act as oxidising or reducing agent depends upon its electrode potential.
- **10.** They are electropositive in nature.
- 11. Most of the transition elements form coloured compounds.
- 12. Their compounds are generally paramagnetic in nature.
- 13. A number of these transition metals and their compounds show catalytic properties.
- 14. They form interstitial compounds with elements like H, C, B and N.
- 15. They form alloys.
- 16. They have a great tendency to form complexes.

#### **6.5 METALLIC CHARACTER**

All the transition elements exhibit all the characteristics of metals. For example they are hard lustrous, malleable and ductile, have high melting and boiling points, high thermal and electrical conductivity and high tensile strength.

Explanation: Transition elements have relatively low ionisation energies and have one or two electrons in their outermost energy level  $(ns^1 \text{ or } ns^2)$ . As a result, metallic bonds arc formed. Hence, they behave as metals. The unpaired d electrons also result in the formation of metallic bonds. Thus, in the formation of metallic bonds, both ns and (n-1) d electrons participate. Greater the number of unpaired d electrons, stronger is the bonding due to the overlapping of unpaired electrons between different metal atoms. Cr, Mo and W have maximum number of unpaired d electrons and are, therefore, hard metals whereas Zn, Cd and Hg are not very hard metals due to the absence of unpaired electrons.

## 6.6 MELTING AND BOILING POINTS

The transition metals have very high melting and boiling points. The melting points of the transition metals rise to a maximum and then fall as the atomic number increases. Manganese and technetium have abnormally low melting points (Fig. 6.1).

Explanation: Strong metallic bonds between the atoms of these elements are responsible for the high melting and boiling points. This is clear from their high enthalpies of atomisation (i.e., heat required to break the metal lattice to get free atoms).

Table 6.3 Enthalpies of atomisation of first transition series.

Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
326	473	575	397	281	416	425	430	339	126

The metals of the second (4d) and third (5d) series have greater enthalpies of atomisation than the corresponding elements of the first series (Fig. 6.2). This is an important factor for their having much more frequent metal-metal bonding in their compounds.

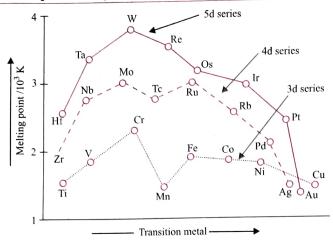


Fig. 6.1 Melting points of transition metals

Greater is the number of unpaired electrons stronger is the metallic bonding. Because of the stronger metallic bonding, these elements have high melting and boiling points.

In a particular series, the metallic strength increases up to the middle with increasing number of unpaired electrons, i.e., up to  $d^5$  configuration. After Cr, the number of unpaired electrons goes on decreasing. Accordingly, the melting points decrease after middle (Cr) because of increasing pairing of electrons.

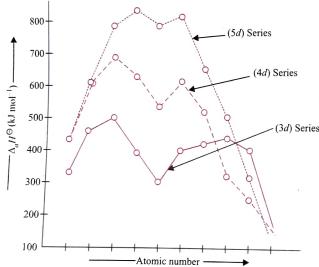


Fig. 6.2 Enthalpies of atomisation of transition metals

**Note:** Note that tungsten (W) has the highest melting point among the d-block elements.

The dip in the melting point at Mn in the first transition series and at Tc in the second transition series and somewhat in Re in the third transition series can be explained on the basis that they have exactly half-filled d-orbitals. As a result, in each case, the electronic configuration is stable, i.e., electrons are held tightly by the nucleus so that the delocalisation is less and the metallic bond is much weaker than that preceding element.

#### **6.7 ATOMIC AND IONIC RADII**

1. The atomic radii of the transition metals lie in-between those of s- and p-block elements.

2. Generally the atomic radii of d-block elements in a series decrease with increase in atomic number but the decrease in atomic size is small after midway. In the first transition series, the atomic radii decrease from Sc to Cr but after that it remains almost same. At the end of the transition series, there is a small increase in atomic radii (Table 6.4).

Table 6.4 Atomic radii of d-block elements in pm

Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu
164	147	135	129	131	126	125	125	128
Y	(Zr)	Nb	Mo	Tc	Ru	Rh	Pd	Ag
180	160	146	129	136	134	134	137	
La	Hf	Ta	W	Re	Os	Ir	Pt	Au
187	158	146	139	137	135	136	138	144

**Note:** Circled elements have almost same atomic radii due to the consequence of lanthanide contraction.

**Explanation:** The observed irregular trend in the atomic radii of the transition metals can be explained by the following factors:

- (i)  $Z_{\rm eff}$  (effective nuclear charge) and (ii) Shielding effect due to increasing number of d-electrons.
- i.  $Z_{\rm eff}$ : In general, transition elements along a given series shows a progressive decrease in the atomic radius due to increase in  $Z_{\rm eff}$ :
- ii. Shielding effect of d-electrons: This is because the extra electron enters a d-orbital each time the nuclear charge increases by unity. The shielding effect of a d-electron is small. The net electrostatic attraction between the nuclear charge and the outermost electron increases and the ionic radius decreases. The atomic radii also decrease in the same way.
- iii. In the beginning, the atomic radius decreases with the increase of atomic number (Z) because of shielding effect of d-electrons is small and increases with increase of d-electrons.
- iv. The decrease within the series is quite small because in atomic radius due to increase in nuclear charge is partly cancelled by the increase in the atomic radius due to shielding effect provided by the electrons being added in the inner d-orbitals.
- v. As a result, the atomic radii remain practically same after chromium. For example, in Fe, the two opposing tendencies almost counterbalance and there is no change in the size from Mn to Fe.

Same type of behaviour is found in second (4d) and third (5d) transition series (Table 6.4).

At the end of the period, there is a slight increase in the atomic radii.

**Explanation:** Near the end of series, the increased electron-electron repulsions between added electrons in the same orbitals are greater than the attractive forces due to the increased nuclear charge. This results in the expansion of the electron cloud and thus the atomic radius increases.

vi. The atomic radii increase down the group. The atomic radii of second (4d) series are larger than those of

 $f_{\text{first}}$  (3d) transition series. But the atomic radii of the  $_{\text{second}}^{\text{mis}}$  (4d) and third (5d) transition are almost the same (Figure 6.3).

Explanation: This is due to the intervention of the 4f orbitals, which must be filled before the 5d series of elements hegin. The filling of 4f before 5d orbitals results in a regular decrease in atomic radii called lanthanoid contraction which compensates for the expected increase in atomic size with increasing atomic number. Thus the increase in normal  $_{\text{size}}$  from  $\text{Sc} \rightarrow \text{Y} \rightarrow \text{La}$  disappears after the lanthanides. The net result of lanthanoid contraction is that the pairs of element such as Zr/Hf, Nb/Ta and Mo/W are almost identical in size. The close similarity of properties in such a pair makes chemical separation very difficult.

The sizes of the third (5d) row of transition elements are very similar to those of the second (4d) row of transition elements. Thus 4d and 5d elements resemble each other more closely than do the first (3d) and second (4d) row.

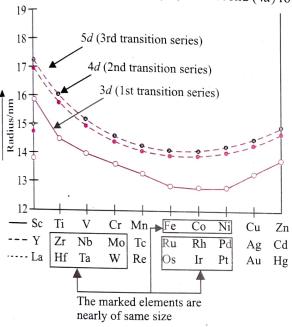


Fig. 6.3 Trends in atomic radii of transition element of lanthanide contraction

#### Ionic radii:

- i. In general, the ionic radii decrease with increase in oxidation state. Thus, the ionic size of M<sup>3+</sup> cations are smaller than those of  $M^{2+}$  cations. This is because the ionic radius decreases with increase in  $(Z_{\rm eff})$  effective nuclear charge. However, the ionic radii of cations in the same oxidation state decrease with the increase in atomic number (see Table 6.5).
- ii. The ionic radii of the transition metals are smaller than those of s and p block elements of the same period.

**Note:** s and p block elements form positive ions, whereas p-block elements form negative ion.

#### ILLUSTRATION 6.2

Why do the transition elements exhibit higher enthalpies of atomisation?

Sol. Because of large number of unpaired electrons in their atoms they have stronger interatomic interaction and hence stronger bonding between atoms resulting in higher enthalpies of atomisation.

#### 6.8 DENSITY

Along the transition series, the decrease in atomic radii or decrease in metallic radius/atomic radius coupled with increase in atomic mass results in general increase in density (Table 6.5).

Thus, from Ti (Z = 22) to Cu(Z = 29) there is a significant increase in the densities of these elements.

Zn is an exception having large atomic volume and hence lower density.

Among d-block elements Sc has lowest (3.43) g cm<sup>-3</sup>) and Ir has highest (22.61 g cm<sup>-3</sup>) densities. Os and Ir have almost same densities.

Table 6.5 Electronic configurations and some other properties of the first series of transition elements

ements		Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
<sup>0mic</sup> number		21	22	23	24	25	26	27	28	29	30
<sup>ectronic</sup> configuration				* E					20	2.9	30
	M	$3d^14s^2$	$3d^24s^2$	$3d^34s^2$	$3d^{5}4s^{1}$	$3d^54s^2$	$3d^64s^2$	$3d^74s^2$	$3d^{8}4s^{2}$	$3d^{10}4s^{1}$	$3d^{10}4s^{-1}$
	1 <sup>⊕</sup>	$3d^14s^1$	$3d^24s^1$	$3d^34s^1$	$3d^5$	$3d^54s^1$	$3d^{6}4s^{1}$	$3d^{7}4s^{1}$	$3d^{8}4s^{1}$	$3d^{10}$	$3d^{10}4s$
	[2+	$3d^1$	$3d^2$	$3d^3$	$3d^4$	$3d^5$	$3d^6$	$3d^7$	$3d^{8}$	3d <sup>9</sup>	$3d^{10}$
M	[3+	$3d^0$	$3d^1$	$3d^2$	$3d^3$	$3d^4$	$3d^5$	3d <sup>6</sup>	$3d^7$	_	_
thalpy of atomisation	$,\Delta_{a}$	<sub>,</sub> H <sup>⊖</sup> /kJ m	$ol^{-1}$								
_		226	473	515	397	281	416	425	430	339	126
<sup>nisation</sup> enthlapy/∆ <sub>i</sub> H	<sup>∋</sup> /k.	J mol <sup>-1</sup>				•					120
HO	I	631	656	650	653	717	762	758	736	745	906
HO	II	1235	1309	1414	1592	1509	1561	1644	1752	1958	1734
	Ш	2393	2657	2833	2990	3260	2962	3243	3402	3556	3829

c	.1	n	Inoversit	_	L		
υ	• 1	v	Inorganic	L.	nem	บรา	1

Metallic / ionic radii / pm					7.127				
M	164	147	135	129	137	126	125	125	128
	104	117		82	82	77	74	70	73
$M^{2+}$	-	dates	79		A LOCAL COLOR	65	61	60	/3
$M^{3+}$	73	67	64	62	65	05			
Standard Electrode Potenti	al $E^{\Theta}/{ m V}$	1	A. A.				1 000		
$M^{2+}/M$		-1.63	-1.18	-0.90	-1.18	-0.44	-0.28	-0.25	+0.34
$M^{3+}/M^{2+}$		-0.37	-0.26	-0.41	+1.57	+0.77	+1.97	- makes	
M°/M°	-	-0.57			7.01	7.8	8.7	8.9	90
Density/g cm <sup>-3</sup>	3.43	4.1	6.07	7.19	7.21	7.0	0.7	0.7	8.9

#### 6.9 OXIDATION STATE

All the transition elements, except the first and last member of the series, show a great variety of oxidation states in its compounds, as shown in Table 6.6.

**Explanation:** The transition elements have a tendency to show variable oxidation states (O.S.) because of very small difference in the energies of (n-1) d and ns orbitals. Therefore, both energy levels are used for chemical bond formation.

In simple compounds, +2 O.S. are obtained by the removal of 2 electrons from ns orbital and (n-1)d remain unaffected. But the higher O.S. like +3, +4, +5, +6 and +7 are obtained by the removal of electrons from both (n-1)d and ns orbitals.

#### Some observations:

- i. The most common O.S. of 3d series elements is +2, except for Sc = +3, +2 O.S. is obtained by the removal of  $ns^2$  electron. This implies that (n-1)d orbitals are more stable than  $ns^2$  orbitals after Sc.
- ii. The number of O.S. shown by the elements along the transition series first increases till middle as the number of unpaired electrons increases after that it starts decreasing as the electrons start getting paired.

- iii. At the other end, the only O.S. of Zn is +2,  $since_{h_0}$  d-electrons are involved (3 $d^{10}$  configuration).
- iv. Maximum value of O.S. for any transition element is found in its compound with F and O, as they are small in size and most EN (electronegative elements).
- v. Transition elements in lower O.S. (i.e. +2 and +3) form ionic compounds while in higher O.S. form covalent compounds (Fazan's rule). Because higher O.S. covalent bonds are formed by sharing d electrons. For example, in MnO<sub>4</sub>  $^{\odot}$  and Cr<sub>2</sub>O<sub>7</sub>  $^{2-}$ , all the bonds formed between Mn and oxygen in MnO<sub>4</sub> and between Cr and oxygen in Cr<sub>2</sub>O<sub>7</sub> are covalent.
- vi. The elements which show the greatest number of oxidation states occur in or near the middle of the series. For example, Mn shows all the oxidation states from +2 to +7. The lesser number of oxidation states on the extreme ends are either due to too few electrons to lose or share (e.g., Sc, Ti) or too many *d*-electrons so that fewer orbitals are available to share electrons with others (e.g., Cu, Zn). The highest oxidation state shown by any transition metal is +8 (by osmium).

**Table 6.6** Generally shown oxidation states of transition metals (very rare oxidation states are given in parentheses and most common ones are enclosed in boxes for first transition series)

							,				
3d Series	Z	21	22	23	24	25	26	27	28	29	
		Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	
			(+2)	+2	+2	+2	+2	+2	+2	+1	
7		+3	+3	+3	+3	+3	+3	+3	+3	+2	
			+4	+4	+4	+4	+4	+4	+4		
				+5	+5	+5					
					+6	+6	-				
					,	+7	(+6)				
4d Series	Z	39	40	41	42	43	44	45	46	47	
		Y	Zr	Nb	Мо	Тс	Ru	Rh	Pd	Ag	_
A 4 4 5 4 5 5 5 5 5 5 5 5 5 5 5 5 5 5 5		+3	(+3)	(+2)	+2	+2	+2	+2	+2	+1	

		+4	1					d- a	nd $f$ - Block E	lements 6.
		14	(+3)	+3	(+4)	+3	+3	(+3)	(+2)	
				(+4)	+4	(+5)	+4	+4	+4	(+3)
				+5	+5		(+5)	(+6)	and the second s	
					+6		(+6)			
							(+7)			
- 2	71						(+8)			
ies 2		72	73	74	75	76	77	78	79	80
	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg
				4	(+1)					
	+3	(+3)	(+2)	+2	(+2)	+2	+2	+2	+1	+1
		+4	(+3)	(+3)	(+3)	+3	+3	(+3)	(+3)	+2
			(+4)	+4	+4	+4	+4	+4		
			+5	+5	+5	+6	(+6)	(+5)		
				+6	(+6)	+8		(+6)		
Silv.					+7				3-92 4	lines of a

- in the maximum oxidation states of reasonable stability in the first transition series is equal to the sum of s and d electrons m to Mn followed by an abrupt decrease in the stability of higher oxidation states.
- The variability of oxidation states of transition elements, which is due to incompletely filled d-orbitals, arises in such a way that successive oxidation states differ by unity, e.g.,  $V^{II}, V^{IV}, V^{V}$ . This is unlike non-transition elements where oxidation states normally differ by two units, e.g., Pb<sup>II</sup>, Pb<sup>IV</sup>, Sn<sup>II</sup>, Sn<sup>IV</sup> etc.
- in line group of d-block elements, the higher oxidation states are more stable for heavier elements.

For example, in group 6, Mo (VI) and W(VI) are found to be more stable than Cr (VI). For this reason, Cr(VI) in the form of dichromate is a stronger oxidising agent in acidic medium whereas MoO3 and WO3 are not. Although in the p-block the lower O.S. are more stable for heavier members due to inert pair effect, e.g. in 13, 14 and 15 groups Tl, Pb and Bi are more stable in +1, +2, and +3 O.S. respectively. For example, the following reaction undergoes reduction hence acts as strong oxidising agent. MoVIO3 and WVIO3 are stable in +6 O.S. and thus do not undergo reduction to give lower O.S. compounds.

$$14H^{\oplus} + Cr_2^{VI}O_7^{2-} + 6e^{\Theta} \longrightarrow 2Cr^{3+} + 7H_2O$$

L. Relative stabilities of transition elements in different O.S. is also determined from their electrode reduction potential value.

For example, Cu exists in +1 and +2 O.S. as Cu<sup>®</sup> and Cu<sup>2+</sup>.

$$\begin{array}{c} \operatorname{Cu}(3d^{10}4s^1) \longrightarrow \operatorname{Cu}^{\oplus}(3d^{10}) + e^{\Theta} \\ \operatorname{Cu}^{\oplus}(3d^{10}) \longrightarrow \operatorname{Cu}^{2+}(3d^9) + e^{\Theta} \\ \operatorname{Cu}^{\oplus}_{(\operatorname{aq})} + e^{\Theta} \longrightarrow \operatorname{Cu}_{(\operatorname{s})} & \dots E_{\operatorname{red}}^{\Theta} = 0.52 \mathrm{V} \\ \operatorname{Cu}^{2+}_{(\operatorname{aq})} + 2e^{\Theta} \longrightarrow \operatorname{Cu}_{(\operatorname{s})} & \dots E_{\operatorname{red}}^{\Theta} = 0.34 \mathrm{V} \end{array}$$

Thus, Cu<sup>2+</sup> is more stable than Cu<sup>®</sup> since

$$E_{\mathrm{Cu}}^{\Theta} \oplus_{(\mathrm{aq})^{/\mathrm{Cu}}(\mathrm{s})} > E_{\mathrm{Cu}^{2+}_{(\mathrm{aq})^{/\mathrm{Cu}_{(\mathrm{s})}}}}^{\Theta}$$

Thus, Cu<sup>⊕</sup> is reduced more easily than Cu<sup>2-</sup>.

- xi. Low oxidation states are found when a complex compound has ligands (like CO) capable of  $\pi$ -acceptor character in addition to the  $\sigma$ -bonding. This is due to synergic bonding. For example, Cu in CuCl is in +1 O.S. whereas Ni in Ni(CO)<sub>4</sub> and Fe in Fe(O)<sub>5</sub> both are in zero O.S.
- xii. The oxidation state of a metal in a solvent depends on the nature of the solvent. The metal in a particular oxidation state may undergo oxidation or reduction in the solvent under appropriate conditions.

For example, Cu<sup>®</sup> is unstable in water it may undergo oxidation whereas Cu<sup>2+</sup> is stable in water. Similarly, Fe<sup>2+</sup> is unstable in aerated water (water -in -which air is dissolved) as it undergoes oxidation in it.

#### ILLUSTRATION 6.3

- a. Phosphorous (P<sub>4</sub>) and vanadium (V) both exhibit variable oxidation states but due to different reason. Explain.
- b. Name the transition metal which does not show variable O.S.

- a. In phosphorous (P<sub>4</sub>) it is due to inert pair effect, whereas in vanadium (V) it is due to the participation of d-orbital
- **b.** Scandium (Sc) (Z = 21);  $3d^{4}4s^{2}$

 $Sc^{2+}$ :  $3d^1 \Rightarrow$  Highly unstable, does not exist.

 $Sc^{3+}$ :  $3d^0 \Rightarrow$  Noble gas configuration, stable and exist.

Therefore Sc shows only +3 O.S.

### **6.10 IONISATION ENTHALPIES (IE)**

### $OR (\Delta_i H^{\odot})$

- 1. There is a gradual increase in ionisation enthalpies (IE) along a transition series from left to right, though some irregularities are observed (Table 6.5).
- 2. The first ionisation enthalpies ( $IE_1$ ) of transition elements lie between s- and p-block elements. They are higher than those of s-block elements and are lower than those of p-block elements.

#### Explanation:

- i. Due to increase in nuclear charge with increase in atomic number (Z), the size of atom decreases and IE (or Δ<sub>i</sub>H<sup>Θ</sup>) increases
- ii. The irregular trend in the  $IE_1$  (or  $\Delta_i H^{\Theta}$ ) of the 3d elements is due to the fact that the removal of electron alters the relative energies of 4s and 3d orbitals. There is thus, a **reorganisation energy** accompanying ionisation. This results into the release of **exchange energy** which increases as the number of d-electrons increases in the  $d^n$  configuration and also from the transference of s-electrons into d-orbitals.
- iii. IE<sub>1</sub> (or  $\Delta_i H_j^{\ominus}$ ) or Cr is lower because there is no change in the *d* configuration and gives stable configuration  $(3d^5)$   $C_{\Gamma}(Z = 24): 3d^54s^1 \longrightarrow Cr^{\oplus}(3d^5) + e^{\ominus}$
- iv. IE<sub>1</sub> (or  $\Delta_i H_1^{\Theta}$ ) of Zn is higher because the electron is lost from 4s level of the stable configuration.

$$Zn (Z = 30):$$
  $3d^{10}4s^2 \longrightarrow Zn^{\oplus}(3d^{10}4s^1) + e^{\Theta}$   
Stable configuration

- **3.** IE<sub>2</sub> and IE<sub>3</sub>, generally increase along the transition series, and usually are much higher, with some exceptions.
  - **Explanation:** Unusually high  $IE_2$  values are due to attainment of stable configuration of  $M^{2+}$  ions in which the configuration of  $M^{\oplus}$  ions are disrupted, with considerable loss of exchange energy. Thus decreasing order of  $IE_2$  of 3d series is

$$Cu > Ni > Zn > Co > Cr > Mn > V > Ti > Sc$$

4. IE<sub>1</sub> of 5d elements are higher those of 3d and 4d elements. This is due to the imperfect (weak) shielding of one electron by another in the same set of orbitals. However, the shielding of one 4f electron by another is less than that of one d-electron by another and as the nuclear charge increases along the series, there is fairly increase in IE<sub>1</sub> of 5d elements. The IE of 3d and 4d elements are irregular.

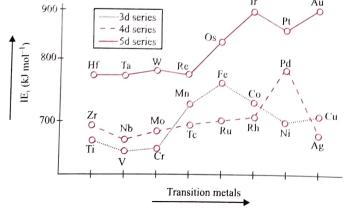


Fig. 6.4 Ionisation enthalpies of transition metals. IE $_1$  of 5d metals are higher than those of 3d and 4d metals

### ILLUSTRATION 6.4

- a. Why IE<sub>1</sub> of Zn, Cd and Hg are very high?
- a. Why IE<sub>1</sub> of 2...
  b. The relative difference in IE of any two consecutive d-block elements is smaller than those of s and p-block elements
- c. IE<sub>2</sub> is unusually very high for Cr and Cu. Why?

#### Sol.

- **a.** It is due to completely filled and stable configuration,  $(n-1) d^{10} ns^2$  configuration.
- b. This is because they involve gradual filling up of inner d-orbitals due to which increase in nuclear charge is partly cancelled by shielding effect provided by "inner d-electrons.
- c. This is because after the removal of first electron  $\operatorname{Cr} \operatorname{and}_{\mathbb{C}_{\parallel}}$  acquire a stable configuration  $(d^5 \operatorname{and} d^{10})$  and the  $\operatorname{rem}_{0V_2}$  of second electron is very difficult.

i. 
$$\operatorname{Cr}(3d^54s^1) \longrightarrow \operatorname{Cr}^{\oplus}(3d^5) + e^{\ominus}$$
 ...  $\operatorname{IE}_1$ 

$$\operatorname{Cr}^{\oplus}(3d^5) \longrightarrow \operatorname{Cr}^{2+}(3d^4) + e^{\ominus}$$
 ...  $\operatorname{IE}_2$ 
(Stable (Less stable configuration) ( $\therefore$   $\operatorname{IE}_2 \gg \operatorname{IE}_1$ )

ii. 
$$\operatorname{Cu}(3d^{10}4s^1) \longrightarrow \operatorname{Cu}^{\oplus}(3d^{10}) + e^{\ominus}$$
 ...  $\operatorname{\mathbb{E}}$ 

$$\operatorname{Cu}^{\oplus}(3d^{10}) \longrightarrow \operatorname{Cu}^{2+}(3d^9) + e^{\ominus} \qquad \dots \operatorname{\mathbb{E}}$$
(Stable (Less stable configuration) configuration) ( $:: \operatorname{\mathbb{E}}_2 >> \operatorname{\mathbb{E}}$ 

#### ILLUSTRATION 6.5

- A.  $IE_2$  for Zn is comparatively lower as compared to  $\mathbb{C}$  and Ni.
- **B.** a. IE<sub>3</sub> of Mn and Zn are very high. Why?
  - b. IE<sub>3</sub> for change from Fe<sup>2+</sup> to Fe<sup>3+</sup> is very small.
  - c. IE<sub>3</sub> of Mn is higher than that of Fe. Why?
  - d. Why Cu, Ni and Zn have a maximum oxidation state of +2?

#### Sol.

**A.** This is because  $Zn^{\oplus}(3d^{10}4s^1)$  will readily lose an electron to acquire stable  $3d^{10}$  configuration.

$$Zn (3d^{10}4s^2) \longrightarrow Zn^{\oplus}(3d^{10}4s^1) + e^{\Theta}$$
 ... 1<sup>E</sup><sub>1</sub>
(Stable (Less stable configuration)
$$Zn^{\oplus} (3d^{10}4s^1) \longrightarrow Zn^{2+}(3d^{10}) + e^{\Theta}$$
(Stable configuration)

- **B.** a. Mn (Z = 25):  $3d^54s^2$  Zn (Z = 30):  $3d^{10}4s^2$ The trend in IE<sub>3</sub> is not complicated by the absence of the orbital in M<sup>2+</sup> ions. This is because after the removal of second electron Mn and Zn acquires stable configuration of  $d^5$  and  $d^{10}$  respectively and hence removal of third electron is very difficult.
  - i.  $\operatorname{Mn}^{2+}(3d^5) \longrightarrow \operatorname{Mn}^{3+}(3d^4) + e^{\Theta}$ (Stable (Less stable configuration)

- ii.  $Zn^{2+}(3d^{10}) \longrightarrow Zn^{3+}(3d^9) + e^{\Theta}$ (Stable (Less stable configuration) (Stable configuration)
- b. This is because the loss of third electron gives the stable configuration  $(d^5)$

Fe (Z = 26): 
$$3d^64s^2$$
  
Fe<sup>2+</sup> ( $3d^6$ )  $\longrightarrow$  Fe<sup>3+</sup>( $3d^5$ ) +  $e^{\Theta}$   
(Stable configuration) ... IE<sub>3</sub>

c. Mn (Z = 25):  $3d^54s^2$ ; Fe (Z = 26):  $3d^64s^2$ Mn<sup>2+</sup>:  $3d^5$  Fe<sup>2+</sup>:  $3d^6$ 

After the removal of second electron,  $Mn^{2+}$  and  $Fe^{2+}$  acquire a configuration of  $3d^4$  and  $3d^5$  respectively. Thus to remove an electron from  $3d^5$  is more difficult than from  $3d^6$ . Hence  $IE_3$  of  $Mn > IE_3$  of Fe.

$$\operatorname{Mn}^{2+}(3d^5) \longrightarrow \operatorname{Mn}^{3+}(3d^4) + e^{\Theta}$$
(Stable configuration) ... IE<sub>3</sub>

$$Fe^{2^+}(3d^6) \longrightarrow Fe^{3^+}(3d^5) + e^{\Theta}$$
(Stable configuration) ...  $IE_3$ 

d. The high values of IE<sub>3</sub> for

Cu 
$$(Z = 29)$$
:  $3d^{10}4s^1$ ; Ni  $(Z = 28)$ :  $3d^84s^2$  and Zn  $(Z = 30)$ :  $3d^{10}4s^2$ 

explains why they have a maximum oxidation of +2.

#### ILLUSTRATION 6,6

- a.  $K_2[Ni^{II}Cl_4]$  exists while corresponding Pt compound  $K_2$  [Pt<sup>II</sup>Cl<sub>4</sub>] is unknown. Why?
- b.  $K_2[Pt^{IV}Cl_6]$  exists while corresponding Ni compound  $K_2$  [Ni $^{IV}Cl_6$ ] is unknown. Why?

#### Sol.

**a.** IE explains about relative stabilities of various oxidation states.

For example,  $Ni^{2+}$  compounds are more stable than  $Pt^{2+}$  compounds, e.g.,

		$IE_1 + IE_2 $ (kJ mol <sup>-1</sup> )
Ni	2.49	Smaller the (IE <sub>1</sub> + IE <sub>2</sub> ) of the metal more
Pt	2.66	stable is its compound.  .: Stability: Ni <sup>2+</sup> > Pt <sup>2+</sup>

In case of Pt high ( $IE_1 + IE_2$ ) value is due to imperfect shielding effect of 4f-orbitals. This shielding effect increases the attraction between nucleus and outermost electron and hence ( $IE_1 + IE_2$ ) of Pt is more.

b.  $(IE_1 + IE_2 + IE_3 + IE_4)$  is lower for Pt.

High (IE<sub>3</sub>+ IE<sub>4</sub>) value for Ni is due to very small size of Ni<sup>3+</sup> and Ni<sup>4+</sup> in comparison to Pt<sup>3+</sup> and Pt<sup>4+</sup>.

Hence stability of Pt<sup>4+</sup> > Ni<sup>4+</sup>.

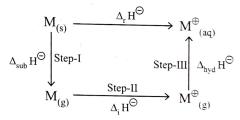
	IE <sub>3</sub> + IE <sub>4</sub>	$ E_1 +  E_2 +  E_3 +  E_4 $ (kJ mol <sup>-1</sup> )
Ni	8.80	2.49 + 8.8 = 11.29
Pt	6.70	2.66 + 6.70 = 9.36

## 6.11 STANDARD ELECTRODE POTENTIAL $(E_{red}^{\circ})$

- 1. Thermodynamic stability of the compounds of transition elements is determined by the magnitude of IE of transition elements. If IE of the element is lower, ore stable is its compounds.
- 2. In solution, the stability of the compounds depends on electrode potential, which depends upon the following factors:
  - **a.** Enthalpy of sublimation of the element  $(\Delta_{\text{sub}} H^{\Theta})$ .
  - **b.** Ionisation enthalpy of the element (IE or  $\Delta_i H$ ).
  - c. Hydration enthalpy of the element  $(\Delta_{hyd}, H^{\circleddash})$
- 3. The total enthalpy of the process  $(M_{(s)} \longrightarrow M^{\oplus}_{(aq)} + e^{\ominus})$  is the sum of three types of enthalpies i.e.,

$$\Delta_r H^{\Theta} = \Delta_{\text{sub.}} H^{\Theta} + \Delta_i H^{\Theta} + \Delta_{\text{hyd}} H^{\Theta}$$

The above steps are represented by Born Haber cycle as follows.



Thus electrode potential is a measure of  $\Delta_r H^{\odot}$ . Hence quantitatively, the stability of transition metal ions in different O.S. is determined by the electrode potential.

The above process represents  $E^{\Theta}_{M(s)/M} \oplus_{(aq)}$ , i.e., oxidation potential and the reverse process i.e.,  $E^{\Theta}_{M} \oplus_{(aq),M(s)}$ , represents the reduction potential. If  $E^{\Theta}_{oxid}$  is more positive, the metal will undergo oxidation more easily and formation of  $M^{\Theta}_{(aq)}$  from  $M_{(s)}$  is more stable.

Similarly, if  $E_{\text{red.}}^{\Theta}$  is more positive, the metal ion will undergo reduction more easily and formation of  $M_{(aq)}^{\Theta}$  from  $M_{(s)}$  is less stable.

Alternatively, the lower the  $E_{\text{red.}}^{\Theta}$  value i.e. more negative  $E_{\text{red.}}^{\Theta}$  i.e. value of the electrode more stable is the oxidation state of the metal in the aqueous solution,

 $E_{\rm M}^{\Theta_{\rm M}^{2+}/M}$  and  $E_{\rm M}^{\Theta_{\rm M}^{3+}/M^{2+}}$  for 3d block elements are given in Table.

The observed and calculated values for  $E^{\Theta}_{M^{2+}/M}$  are compared in following Figure 6.5.

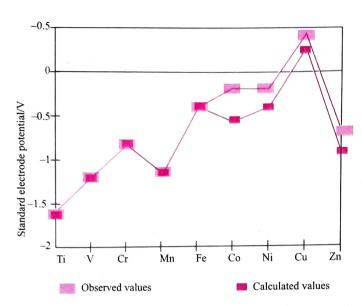


Fig. 6.5 Observed and calculated values for the standard electrode potentials ( $M^{2+} \longrightarrow M^0$ ) of elements Ti to Zn

**Table 6.7** Thermochemical data (kJ mol<sup>-1</sup>) for the 3d series of transition elements and the standard electrode potentials for the reduction of M<sup>II</sup> to M

Element (M)	$\Delta_a H^{\Theta}(M)$	$\Delta_i \mathbf{H_1}^{\ominus}$	$\Delta_i H_2^{\Theta}$	$\Delta_{\rm hyd}{\rm H}^{\odot}({\rm M}^{2+})$	E <sup>⊙</sup> /V
Ti	469	661	1310	-1866	-1.63
V	515	648	1370	-1895	-1.18
Cr	398	653	1590	-1925	-0.90
Mn	279	716	1510	-1862	-1.18
Fe	418	762	1560	-1998	-0.44
Co	427	757	1640	-2079	-0.28
Ni	431	736	1750	-2121	-0.25
Cu	339	745	1960	-2121	+0.34
Zn	130	908	1730	-2059	-0.76

## 6.11.1 TRENDS IN THE $E^{\odot}_{(\mathrm{M}^{2+}/\mathrm{M})}$ VALUES IN 3d Series

- 1. There is no regular trend in the  $E^{\Theta}_{(M^{2+}/M)}$  values of 3d series (Table 6.5), because sum of ( $IE_1 + IE_2$ ) and  $\Delta_{\text{sub.}}H^{\Theta}$  do not show any regular trend.
- 2. The general trend towards less negative  $E^{\ominus}_{(M^{2+}/M)}$  values along the 3d series (except for  $E^{\ominus}_{(Cu^{2+}/Cu)}$  values) is due to general increase in the sum of (IE $_1$  + IE $_2$ ) values.
- 3. Copper (Cu) is the only metal in 3d series which have positive  $E^{\Theta}_{\text{Cu}^{2+}(\text{aq})/\text{Cu(s)}}$  value, because high sum of

 $(IE_1 + IE_2 + \Delta_{sub}, H^{\Theta})$  values is not counterbalanced by low  $\Delta_{hyd}, H^{\Theta}$  value.

The positive  $E^{\Theta}_{\text{Cu}^{2+}(\text{aq})/\text{Cu(s)}}$  value suggests that reduction of  $\text{Cu}^{2+}_{\text{(aq)}}$  to  $\text{Cu}_{\text{(s)}}$  is favourable. For example,

$$Cu_{(s)} \xrightarrow{\Delta_{sub} H^{\odot}} Cu^{2+}_{(aq)}$$

$$\downarrow \qquad \qquad \downarrow \qquad \qquad \qquad \downarrow \qquad \qquad \qquad \downarrow \qquad \qquad \qquad \downarrow \qquad \qquad \qquad \downarrow \qquad \qquad \qquad \downarrow \qquad \qquad$$

If the oxidation reaction from  $Cu_{(s)}$  to  $Cu^{2^+}_{(aq)}$  is  $favourabl_{\ell_i}$  then it should have low sum of  $(IE_1 + IE_2 + + \Delta_{sub_i} H^{\Theta})_{value_i}$  and more negative  $\Delta_{hyd.} H^{\Theta}$  value.

But the reverse process i.e. reduction of  $Cu^{2+}_{(aq)}$  to  $Cu_{(s_1)}^{1+}$  favourable because of high sum of  $(IE_1 + IE_2 + \Delta_{sub}^{(s_1)})$  values and less negative  $\Delta_{hyd}H^{\Theta}$  value.

4.  $E^{\Theta}_{M^{2+}(aq)/Mn(s)}$  values of all the transition elements (except Cu in 3d series) is lower (negative) than that of hydrogen (taken as zero). Thus all the transition elements, with negative reduction potential liberate  $H_{2(g)}$  from dilute acids. But Cu does not liberate  $H_{2(g)}$  from dilute acids. Cu is inent towards non-oxidising acids, but reacts with conc.  $HNO_{2}$  and  $H_{2}SO_{4}$ .

$$3Cu + 8HNO_3 \longrightarrow 2NO_{(g)} + 3Cu(NO_3)_2 + 4H_2O$$
Dilute

Cu + 4HNO - > 2NO - + G 2VO - - 2VO

$$\text{Cu} + 4\text{HNO}_3 \longrightarrow 2\text{NO}_{2(g)} + \text{Cu(NO}_3)_2 + 2\text{H}_2\text{O}_3$$
  
Conc.

5. The value of  $E_{M^{2+}(aq)/M(s)}^{\ominus}$  for Mn, Ni and Zn are more negative than expected from the general trend (Table 6.5). This is due to greater stability of half-filled d-subshell (d) in Mn<sup>2+</sup> and completely filled d-subshell (d<sup>10</sup>) in Zn<sup>2+</sup>, e.g.

i. 
$$\operatorname{Mn}(Z = 25) (3d^54s^2) \longrightarrow \operatorname{Mn}^{2+} (3d^5) \dots \operatorname{E}_{\text{red}}^{\Theta} = -1.18V$$
(Stable)

ii. 
$$Zn (Z = 30) (3d^{10}4s^2) \longrightarrow Zn^{2+} (3d^{10}) \dots E^{\Theta} = -0.76V$$
(Stable)

iii. The exceptional  $E^{\Theta}_{\mathrm{Ni}^{+}(\mathrm{aq})/\mathrm{Ni}(\mathrm{s})}$  value from the regular trend is due to its high negative  $\Delta_{\mathrm{hvd}}H^{\Theta}$  value.

#### ILLUSTRATION 6.7

Why is  $Cr^{2+}$  reducing and  $Mn^{3+}$  oxidising when both have disconfiguration?

Sol. 
$$\operatorname{Cr}(Z = 24) = 3d^54s^1$$
  $\operatorname{Cr}^{2+} = 3d^4$   $\operatorname{Cr}^{2+}(3d^4) \longrightarrow \operatorname{Cr}^{3+}(3d^3) + e^{\Theta}$  [Undergo oxidation  $t_{2g}^3$  and thus is reducing] (More stable configuration)

 $Cr^{2+}$  undergoes oxidation and hence is reducing as its configuration changes from  $d^4$  to  $d^3$ , the latter having a half filled  $t_{2g}^3$  level. On the other hand, the reduction of  $Mn^{3+}$  to  $Mn^{2+}$  results in the half-filled  $(3d^5)$  configuration which has extra stability, and thus is oxidising.

Mn 
$$(Z = 25) = 3d^54s^2$$
,  $Mn^{2+} = 3d^5$ ,  $Mn^{3+} = 3d^4$   
 $Mn^{3+}(3d^4) + e^{\Theta} \longrightarrow Mn^{2+}(3d^5)$ 

(More stable configuration)

[Undergo reduction and thus is oxidising]

## 6.11.2 TRENDS IN THE $E^{\odot}_{(M^{3+}(aq)/M^{2+}(aq))}$ VALUES OF 3d SERIES

 $E^{\Theta_{(M^{3^{+}}/M^{2^{+}})}}$  values of 3d-elements show the varying trends. (Table  $E^{\Theta_{(M^{3^{+}}/M^{2^{+}})}}$  value shows that reduction of 6.5). More high positive  $(E^{\Theta_{(M^{3^{+}}/M^{2^{+}})}})$  value shows that reduction of  $M^{3^{+}}$  occurs very easily. This accounts for stronger oxidising properties of  $M^{3^{+}}$  ion.

1. The very low value for  $E^{\Theta}_{(Sc^{3+}/Sc^{2+})}$  is due to stable noble gas configuration of  $Sc^{3+}$  ion.

$$\frac{gas}{Sc}(Z = 21) = 3d^{1}4s^{2}, \quad Sc^{2+} = 3d^{1}, \quad Sc^{3+} = 3d^{0}$$

$$\frac{gas}{Sc}(Z = 21) = 3d^{1}4s^{2}, \quad Sc^{2+} = 3d^{1}, \quad Sc^{3+} = 3d^{0}$$

(Stable configuration)

2. The comparatively low negative value for

 $E^{\Theta}_{V^{3+}/V^{2+}} = -0.26V$ , is due to half stable  $t_{2g}^3$  configuration of  $V^{2+}$  ion.

$$V(Z = 23) = 3d^34s^2, V^{2+} = 3d^3, V^{3+} = 3d^2$$
  
 $V^{3+}(3d^2) + e^{\Theta} \longrightarrow V^{2+}(3d^3)(t_{2g}^3)$   
(Stable configuration)

3. The comparatively high negative  $E_{\text{Cr}^{3+}/\text{Cr}^{2+}}^{\Theta} = -0.41\text{V}$ , is due to more stable configuration of  $\text{Cr}^{3+}$  ion having a half-filled  $t_{2\pi}^3$  level.

$$\operatorname{Cr}^{3+}(3d^3) + e^{\Theta} \longrightarrow \operatorname{Cr}^{2+}(3d^4)$$

(More stable

(Less stable

 $t_{2g}^3$  configuration)

configuration

4. The comparatively high positive value for  $E^{\Theta}_{(Mn^{3+}/Mn^{2+})}$  = +1.57V, is due to very stable ( $d^{5}$ ) configuration of  $Mn^{2+}$  ion.

Mn 
$$(Z = 25) = 3d^54s^2$$
, Mn<sup>2+</sup> =  $3d^5$ , Mn<sup>3+</sup> =  $3d^4$   
Mn<sup>3+</sup> $(3d^4) + e^{\Theta} \longrightarrow \text{Mn}^{2+}(3d^5)$   
(Stable configuration)

5. The comparatively low positive value for  $E^{\odot}_{(Fe^{3+}/Fe^{2+})}$  = + 0.77V, is due to stable configuration of Fe<sup>3+</sup> (3 $d^5$ ) ion.

Fe 
$$(Z = 26) = 3d^64s^2$$
, Fe<sup>2+</sup> =  $3d^6$ , Fe<sup>3+</sup> =  $3d^5$ 

$$Fe^{3+}(3d^5) + e^{\Theta} \longrightarrow Fe^{2+}(3d^6)$$

(Stable

configuration)

Although from electronic configuration, reduction of Fe<sup>3+</sup>  $(d^5)$  to Fe<sup>2+</sup>  $(d^6)$  is not very favourable yet low positive  $E_{\text{red}}^{\Theta}$  value favours the reduction of Fe<sup>3+</sup> to Fe<sup>2+</sup> ion to some extent

Due to high charge density of  $Fe^{3+}$  ion, high (negative) hydration enthalpy  $(\Delta_{hyd.}H^{\Theta})$  favours the reduction of  $Fe^{3+}$  to  $Fe^{2+}$  ion

6. Exceptional high positive  $E^{\Theta}_{(Co^{3+}/Co^{2+})}$  (+1.97V) value cannot be explained satisfactorily by electronic configuration

Co 
$$(Z = 27) = 3d^7 4s^2$$
; Co<sup>2+</sup> =  $3d^7$ , Co<sup>3+</sup> =  $3d^6$   
Co<sup>3+</sup> $(3d^6) + e^{\Theta} \longrightarrow Co^{2+}(3d^7)$ 

The stabilities of  $d^6$  and  $d^7$  configuration cannot be compared. The extra stability of  $Co^{2+}$  ( $d^7$ ) configuration

and high positive  $E^{\Theta}_{\text{Co}^{3+}/\text{Co}^{2+}}$  value is related to the highest negative enthalpy of hydration  $(\Delta_{\text{hyd}}, \text{H}^{\Theta})$ . In 3d series, size of  $\text{Co}^{3+}$  ion is 61 pm, therefore charge density is very high. Hence have highest negative  $\Delta_{\text{hyd}}, \text{H}^{\Theta}$  value.

- 7. Similarly, high positive  $E^{\Theta}_{\text{Ni}^{3+}/\text{Ni}^{2+}}$  value can be related to the high negative enthalpy of hydration  $(\Delta_{\text{hyd.}} \text{H}^{\Theta})$ .
- **8.** The highest positive value (not given in Table 6.5) of  $E^{\bigodot}_{(Zn^{3+}/Zn^{2+})}$  is due to very high stable full filled  $(3d^{10})$  configuration of  $Zn^{2+}$  ion.

Zn (Z = 30) = 
$$3d^{10}4s^2$$
; Zn<sup>2+</sup> =  $3d^{10}$ , Zn<sup>3+</sup> =  $3d^{9}$   
Zn<sup>3+</sup>( $3d^{9}$ ) +  $e^{\Theta}$   $\longrightarrow$  Zn<sup>2+</sup>( $3d^{10}$ )

(Very stable configuration)

It is difficult to remove an electron from  $Zn^{2+}$  ion to change it into +3 state.

## 6.12 CHEMICAL REACTIVITY AND E<sup>®</sup> VALUES

The transition metals vary widely in their chemical reactivity. Some of them are highly electropositive and dissolve in mineral acids whereas a few of them are 'noble', i.e., they do not react with simple acids.

Some results of chemical reactivity of transition metals as related to their  $E^{\circ}$  values are given below:

- 1. The metals of the 3d-series (except copper) are relatively more reactive than the other series. Thus, they are oxidised by H<sup>⊕</sup>ions though the actual rate is slow, e.g., Ti and V are passive to dilute non-oxidising acids at room temperature.
- **2.** Less negative  $E^{\odot}$  values for  $\text{Mn}^{2+}/\text{Mn}$  along the series indicate a decreasing tendency to form divalent cations.
- 3. More, negative  $E^{\Theta}$  values than expected for Mn, Ni and Zn show greater stability for Mn<sup>2+</sup>, Ni<sup>2+</sup> and Zn<sup>2+</sup>.
- 4.  $E^{\Theta}$  values for the redox couple  $M^{3+}/M^{2+}$  indicate that  $Mn^{3+}$  and  $Co^{3+}$  ions are the strongest oxidising agents in aqueous solution whereas  $Ti^{2+}$ ,  $V^{2+}$  and  $Cr^{2+}$  are strongest reducing agents and can liberate hydrogen from a dilute acid, e.g.,  $2Cr^{2+}_{(aq)} + 2H^{\oplus}_{(aq)} \longrightarrow 2Cr^{3+}_{(aq)} + H_{2(g)}$

#### ILLUSTRATION 6.8

For the first row transition metals the  $E^{\Theta}$  values are:

 $E^{\odot}$  V Cr Mn Fe Co Ni Cu  $(M^{2+}/M)$  -1.18 -0.91 -1.18 -0.44 -0.28 -0.25 +0.34 Explain the irregularity in the above values.

Soil. The  $E^{\Theta}$  (M<sup>2+</sup>/M) values are not regular which can be explained from the regular variation of ionisation enthalpies ( $\Delta_i H_1 + \Delta_i H_2$ ) and also the sublimation enthalpies which are relatively much less for manganese and vanadium.

#### ILLUSTRATION 6.9

Why is the value for the  $Mn^{3+}/Mn^{2+}$  couple much more positive than that for  $Cr^{3+}/Cr^{2+}$  or  $Fe^{3+}/Fe^{2+}$ ? Explain.

#### Sol. Refer to Section 6.11.2, points (3), (4) and (5).

Much larger third ionisation energy of Mn (where the required change is  $d^5$  to  $d^4$ ) is mainly responsible for this. This also explains why the +3 state of Mn is of little importance.

$$E_{\text{Mn}^{3+}/\text{Mn}^{2+}}^{\Theta} > E_{\text{Fe}^{3+}/\text{Fe}^{2+}}^{\Theta} > E_{\text{Cr}^{3+}/\text{Cr}^{2+}}^{\Theta}$$
 $(+1.57 > +0.77 > -0.41\text{V})$ 

## 6.13 TRENDS IN STABILITY OF HIGHER OXIDATION STATES OF TRANSITION METAL HALIDES

The stable halides of the 3d series of transition metals are shown in table given below.

Table 6.8 Formulas of halides of 3d metals

+6	No. of		CrF <sub>6</sub>		44	le de la constitución de la cons	111_		ed est
+5		VF <sub>5</sub>	CrF <sub>6</sub>	P.	1		1,2		
+4	TiX <sub>4</sub>	$VX_4^I$	CrX <sub>4</sub>	MnF <sub>4</sub>	1				
+3	TiX <sub>3</sub>	VX <sub>3</sub>	CrX <sub>3</sub>	MnF <sub>3</sub>	FeX <sub>3</sub> <sup>I</sup>	CoF <sub>3</sub>			
+2	TiX <sub>2</sub> <sup>III</sup>	VX <sub>2</sub>	CrX <sub>2</sub>	$MnX_2$	FeX <sub>2</sub>	CoX <sub>2</sub>	NiX <sub>2</sub> <sup>II</sup>	CuX <sub>2</sub> <sup>II</sup>	ZnX
+1								CuX <sup>III</sup>	

i The highest oxidation states vary from +4 for Ti (in TIX<sub>4</sub>, tetrahalides) to +5 for V (VF<sub>5</sub>) to +6 for Cr (in CrF<sub>6</sub>), then to +7 for Mn (not in simple halides but in MnO<sub>3</sub>F). Beyond Mn, no metal shows an oxidation state of more than +3, which is only in the trihalides, FeX<sub>3</sub> and CoF<sub>3</sub>.

The highest oxidation is generally most stable with fluorine. This is due to either higher lattice energy, e.g., in CoF<sub>3</sub> or

- higher bond enthalpies for the higher covalent compounds, e.g., in VF<sub>5</sub> and CrF<sub>6</sub>.
- ii. V directly shows an oxidation state of + 5 only in VF<sub>5</sub>, other halides, however, undergo hydrolysis to give oxohalides, VOX<sub>3</sub> in which oxidation state of V is +5.
- iii. In the low oxidation states, fluorides are unstable, e.g., in TIX<sub>2</sub>, VX<sub>2</sub>, CuX ( $X = CI^{\bigcirc}$ ,  $Br^{\bigcirc}$ ,  $I^{\bigcirc}$ ), but not  $F^{\bigcirc}$ . However, copper(II) halides are known including  $CuF_2$  but except iodide. They oxidise iodide to iodine

$$2Cu^{2+} + 4I^{\bigodot} \xrightarrow{} Cu_2I_{2(s)} + I_2$$
 Cuprous iodide

#### That is why Cu<sub>2</sub>I<sub>2</sub> exists but CuI<sub>2</sub> does not.

iv. Many copper(I) compounds are unstable in aqueous solution and undergo disproportionation as follows:

$$2Cu^{\oplus} \longrightarrow Cu^{2+} + Cu$$

The greater stability of  $Cu^{2+}_{(aq)}$  than  $Cu^{\oplus}_{(aq)}$  is due to much more negative enthalpy of hydration for  $Cu^{2+}_{(aq)}$  than  $Cu^{\oplus}_{(aq)}$ . This more than compensates for the high  $IE_2$  of Cu.

## 6.13.1 OXIDES OF 3d ELEMENTS AND THEIR STABILITY

Oxygen stabilises the highest oxidation state in its oxide.

- i. The highest oxidation number in the oxides is same as that of group number and is attained in Sc<sub>2</sub>O<sub>3</sub> to Mn<sub>2</sub>O<sub>7</sub> i.e. up to group 7.
- ii. Beyond group 7, the maximum oxidation is + 3 (in Fe<sub>2</sub>O<sub>3</sub>), although in the ferrates,  $(\text{FeO}_4)^{2^-}$ , formed in the alkaline medium, Fe has oxidation state of + 6. But these readily decompose to Fe<sub>2</sub>O<sub>3</sub> and O<sub>2</sub>.
- iii. Besides the oxides, higher oxidation states are also found in the oxocations, e.g.,  $V^{5+}$  in  $VO_2^{\oplus}$ ,  $V^{6+}$  in  $VO^{2+}$  and  $T^{4+}$  in  $TiO^{2+}$ .

Table 6.9 Oxides of 3d metals

Oxidation					Groups							
number	3	4	5	6	7	8	9	10	11	12		
	Sc	Ti	V	Cr	Cr	Cr	Mn	Fe	Co	Ni	Cu	Zn
+7	7.				Mn <sub>2</sub> O <sub>7</sub>							
+6				CrO <sub>3</sub>			7 18 1	7 7 8 7 7 7 7 7 7 7 7 7 7 7 7 7 7 7 7 7				
+5		A	V <sub>2</sub> O <sub>5</sub>		1 2 32 "							
+4		TiO <sub>2</sub>	V <sub>2</sub> O <sub>4</sub>	CrO <sub>2</sub>	MnO <sub>2</sub>							
+3	$Sc_2O_3$	Ti <sub>2</sub> O <sub>3</sub>	$V_2O_3$	Cr <sub>2</sub> O <sub>3</sub>	Mn <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>		,				
					Mn <sub>3</sub> O <sub>4</sub>	Fe <sub>3</sub> O <sub>4</sub> *	Co <sub>3</sub> O <sub>4</sub> *		alama ye a a			
+2		TiO	VO ,	(CrO)	MnO	FeO	CoO	NiO	CuO	ZnC		
+1			S		1 1	1.1.1.2			Cu <sub>2</sub> O			

6.13.2 MnF<sub>4</sub> AND Mn<sub>2</sub>O<sub>7</sub> EXISTS BUT MnF<sub>7</sub> DOES NOT

The highest Mn fluoride is MnF<sub>4</sub>, whereas the highest oxide is  $Mn_2O_7$ . In other words in Mn fluoride the highest oxidation state of Mi is +4 but in oxides it is +7, although F is more EN than oxygen.

the ability of oxygen to stabilise these high oxidation states that of fluorine. This is due to the ability of an include heart of the ability of an include the ability of oxygen to the ability of oxygen to multiple bonds to metals. Vacant 3d-orbital that to the ability of oxygen to metals. Vacant 3*d*-orbitals of Mn multiple bonds to metals. Vacant 3*d*-orbitals of Mn multiple bonds to metals.  $(p\pi - d\pi)$ vacant 3d-orbitals of Mn with 2p-orbitals of oxygen to form  $(p\pi - d\pi)$  multiple bonds in Figure.

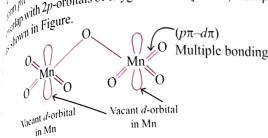


Fig. 6.6 Structure of Mn<sub>2</sub>0<sub>7</sub>

## LUSTRATION 6.10

How would you account for the increasing oxidising power in How we have  $VO_2^{\oplus} < Cr_2O_7^{2-} < MnO_4^{\ominus}?$ 

This is due to the increasing stability of the lower species which they are reduced.

 $_{i, Mn}^{N} O_{4}^{\Theta}$  is reduced to more stable configuration Mn<sup>2+</sup>(3 $d^5$ ) and Mn<sup>4+</sup>  $(3d^3 \text{ or } t^3_{2g})$ .

Hence, it acts as strongest oxidising agent amongst the given

 $_{\rm li.}$  Cr<sub>2</sub>  $^{\rm VII}$ O<sub>7</sub>  $^{\rm 2-}$  is reduced to a stable configuration  ${\rm Cr}^{3+}$  (3 $d^3$  or  $\frac{1}{2}$ . Hence it acts as a stronger oxidising agent.

 $\ln (V^V O_2)^{\oplus}$ , V is in +5 O.S. having  $3d^0$  stable configuration and is therefore not reduced effectively.

Thus, the increasing oxidising power is as follows:

$$VO_2^{\oplus} < Cr_2O_7^{2-} < MnO_4^{\ominus}$$

### 6.14 MAGNETIC PROPERTIES

Each element has some kind of magnetic properties associated with it. These properties have direct consequence of the electronic unfiguration of the atom. When a magnetic field is applied to substances, mainly two types of magnetic behaviour are observed: Diamagnetism and (ii) Paramagnetism.

- 1. Diamagnetic substances are weakly repelled by the magnetic applied field and have all the electrons paired in their atoms, e.g. NaCl and H<sub>2</sub>O.
- 2. Paramagnetic substances are attracted by the magnetic applied field and has one or more unpaired electrons in their atoms, e.g.  $Cu^{2+}$ ,  $Fe^{3+}$ ,  $Cr^{3+}$  and  $O_2$ .

Substances which are strongly attracted by the magnetic applied field are said to be ferromagnetic. In fact, ferromagnetism is an extreme form of paramagnetism.

3. Ferromagnetic substances keep their magnetism even after the field is removed while paramagnetic and diamagnetic substances fail to do so. Fe, Co and Ni are some examples <sup>0f</sup> ferromagnetic substances.

4. Paramagnetism is due to the presence of unpaired electrons. An electron in an atom which has two types of motion, one of its motion is about the nucleus (orbital angular momentum), and the other is its spin about its own axis (spin angular momentum).

A single electron, spinning about its own axis .generates a magnetic field. For two electrons in an orbital, the spins are opposite and hence the fields cancel each other, hence they have zero magnetic moment value.

- 5. When there are one or more unpaired electrons in them, the unpaired electron gives rise to a magnetic field on account of its spin and because of the angular orbital moment.
- **6.** Magnetic moment  $(\mu_{S+L})$  of the first row of transition metal ions is given by general formula:

$$\mu_{S+L} = \sqrt{4S(S+1) + L(L+1)}$$

where S is the sum of spin quantum numbers and L = sumof the orbital angular momentum quantum numbers.

For an electron, spin quantum number,  $S = \pm 1/2$ . Hence, S $= s \times n$  (n = number of unpaired electrons).

For the compounds of the first series of transition metals, the contribution of the orbital angular momentum is effectively quenched and hence is of no significance. For these the magnetic moment is determined by the number of unpaired electrons and is calculated by using 'spin **only' formula.** Taking L = 0, the magnetic moment is given

$$\mu_s = \sqrt{4S(S+1)}$$

In terms of n (number of unpaired electrons), it is given by

$$\mu_s = \sqrt{n(n+2)}$$
 BM (Bohr magneton)

7. It is measured in BM.

1 BM = 
$$\frac{eh}{4\pi m}$$
 = 9.27 × 10<sup>-21</sup> ergs gauss<sup>-1</sup>  
or 9.27 × 10<sup>-24</sup> × J Tesla<sup>-1</sup> or 9.27 × 10<sup>-24</sup> A m<sup>2</sup>

where h is the Planck's constant, e is the electronic charge, and m is the mass of electrons.

Note: The orbital motion in 4f orbitals is not quenched, as in the case of d-block elements. Hence the observed paramagnetism in 4 f-block elements is due to both orbital motion of the electron and its spinning round its axis.

When 
$$n = 1, \mu_s = \sqrt{1(1+2)} = \sqrt{3} = 1.73 \text{ BM}$$
  
 $n = 2, \mu_s = \sqrt{2(2+2)} = \sqrt{8} = 2.83 \text{ BM}$   
 $n = 3, \mu_s = \sqrt{3(3+2)} = \sqrt{15} = 3.87 \text{ BM}$ 

and so on.

 $\therefore \mu_s \propto n$  (number of unpaired electrons).

The magnetic moments calculated from the 'spin-only' formula and those derived experimentally for some of the ions of the first row transition elements are given in Table. The experimental data are mainly for hydrated ions in solution or in the solid state.

Table 6.10 Magnetic moments of some ions of 3d-series

lons	Configuration	Unpaired	Magnetic moment (BM)		
Sc <sup>3+</sup>	$Sc = 3d^{1}4s^{2}$	electron(s)	Calculated		
(Z = 21)	$\Rightarrow Sc^{3+} = 3d^04s^0$	0	$\mu_s = \sqrt{n(n+2)} = 0$	Obser 0	
$Ti^{3+}$ $(Z=22)$	$To = 3d^24s^2$ $\Rightarrow Ti^{3+} = 3d^14s^0$	1	$\sqrt{1(1+2)} = \sqrt{3} = 1.73$	1.75	
$Ti^{2+}$ $(Z=22)$	$Ti = 3d^24s^2$ $\Rightarrow Ti^{2+} = 3d^24s^0$	2	$\sqrt{2(2+2)} = \sqrt{8} = 2.84$	2.76	
$V^{2+}$ $(Z=23)$	$V = 3d^3 4s^2$ $\Rightarrow V^{2+} = 3d^3 4s^0$	3	$\sqrt{3(3+2)} = \sqrt{15} = 3.87$	3.86	
$Cr^{2+}$ (Z = 24)	$Cr = 3d^54s^1$ $\Rightarrow Cr^{2+} = 3d^44s^0$	4	$\sqrt{4(4+2)} = \sqrt{24} = 4.90$	4.80	
$Mn^{2+}$ $(Z=25)$	$Mn = 3d^54s^2$ $\Rightarrow Mn^{2+} = 3d^54s^0$	5	$\sqrt{5(5+2)} = \sqrt{35} = 5.92$	5.96	
$Fe^{2+}$ (Z = 26)	Fe = $3d^64s^2$	4	$\sqrt{4(4+2)} = \sqrt{24} = 4.90$	5.3–5	
$Co^{2+}$ $(Z=27)$	$Co = 3d^{7}4s^{2}$ $\Rightarrow Co^{2+} = 3d^{7}4s^{0}$ $\begin{vmatrix} 3d & 4s \\ 1 & 1 & 1 & 1 \\  & 1 & 1 & 1 \\  & 1 & 1$	3	$\sqrt{3(3+2)} = \sqrt{15} = 3.87$	4.4-5	
$Ni^{2+}$ (Z = 28)	Ni = $3d^{8}4s^{0}$	2	$\sqrt{2(2+2)} = \sqrt{8} = 2.84$	2.9–3	
$Cu^{2+}$ $Z = 29$	$Cu = 3d^{10}4s^{1} \Rightarrow Cu^{2+} = 3d^{9}$ $\boxed{1   1   1   1   1}$	1	$\sqrt{1(1+2)} = \sqrt{3} = 1.73$	1.8–2	
$Zn^{2+}$ $Z = 30$	$Zn = 3d^{10}4s^2 \Rightarrow Zn^{2+} = 3d^{10}4s^0$ $1   1   1   1   1   1  $	0	$\sqrt{0(0+2)} = 0$	0	

#### ILLUSTRATION 6.11

Which element in 3d, 4d and 5d transition series has the highest paramagnetism in:

a. elemental form

b. + 1 O.S.

c. +20.5.

d. + 3 O.S.

, 50.5.

[O.S. = Oxidation State]

#### Sol.

Group	3	4	5	6	7	8	9	10	11	12
3 <i>d</i>	21	22	23	24	25	26	27	28	29	30
1.75	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zr
4 <i>d</i>	39	40	41	42	43	44	45	46	47	48
	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cc
5d	57	72	73	74	75	76	77	78	79	80
	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Не

#### a. In elemental form:

3d series: Cr  $(Z = 24) \Rightarrow 3d^54s^1$ ; n = 6,

 $\mu = \sqrt{6 + (6 + 2)} = \sqrt{48} \text{ BM}$ 

4d series: Mo  $(Z = 42) \Rightarrow 4d^56s^1$ , n = 6,  $\mu = \sqrt{48}$  BM

**5d** series: W  $(Z = 74) \Rightarrow 5d^45s^2$ ; n = 4,  $\mu = \sqrt{24}$  BM

But Re has the highest number of unpaired electron, as shown:

Re 
$$(Z = 75) \Rightarrow 5d^56s^2$$
;  $n = 5$ ,  $\mu = \sqrt{35}$  BM

#### b. In +1 oxidation state:

3d series: Mn  $(Z = 25) \Rightarrow 3d^54s^2$ ; Mn<sup>1+</sup> =  $3d^54s^1$ 

 $n = 6, \ \mu = \sqrt{48} \text{ BM}$ 

4d series: Tc  $(Z = 43) \Rightarrow 4d^55s^2$ ; Tc<sup>1+</sup> =  $4d^55s^1$ 

 $n = 6, \ \mu = \sqrt{48} \ \text{BM}$ 

**5d series:** Re  $(Z = 75) \Rightarrow 5d^56s^2$ ; Re<sup>1+</sup> =  $5d^56s^1$ n = 6,  $\mu = \sqrt{48}$  BM

c. In +2 oxidation state:

3d series: Mn  $(Z = 25) \Rightarrow 3d^54s^2$ ; Mn<sup>2+</sup> =  $3d^54s^0$ 

 $n = 5, \ \mu = \sqrt{35} \text{ BM}$ 

**4d series:** Tc  $(Z = 43) \Rightarrow 4d^55s^2$ ; Tc<sup>2+</sup> =  $4d^55s^0$ 

 $n = 5, \ \mu = \sqrt{35} \ \text{BM}$ 

**5d series:** Re  $(Z = 75) \Rightarrow 5d^56s^2$ ; Re<sup>2+</sup> =  $5d^56s^0$ 

 $n = 5, \ \mu = \sqrt{35} \ \text{BM}$ 

#### d. In +3 oxidation state:

**3d series:** Fe  $(Z = 26) \Rightarrow 3d^64s^2$ ; Fe<sup>3+</sup> =  $3d^54s^0$ 

We write: Ru (Z = 44)  $\Rightarrow$  4d 5s<sup>1</sup> (exception electronic sometimation) Ru = 4d 5s<sup>0</sup>; n = 5,  $\mu = \sqrt{35}$  BM

From the above calculations it is clear that in the elemental form (zero O.S.), group 6 has the highest  $\mu$ , except W, in 5d series, but it is Re of group 7.

1 ln +1 O.S., group 7 has the highest μ.

 $_{\rm HL}$  In +2 O.S., again group 7 has the highest  $\mu$ .

 $\ln +3$  O.S., group 8 has the highest  $\mu$ .

## LUSTRATION 6.12

Calculate the magnetic moment of a divalent ion in aqueous channel if its atomic number is 25.

With atomic number 25, the divalent ion in aqueous will have  $a^{\frac{1}{2}}$  configuration (five unpaired electrons). The magnetic moment  $\mu$  is

$$u = \sqrt{5(5+2)} = 5.92 \text{ BM}$$

## 6.15 FORMATION OF COLOURED IONS

Must of the transition metal compounds ionic and covalent are minuted both in solid and aqueous solution in visible light. When m electron from a lower energy d orbital is excited to a inite energy d orbital, the energy of excitation corresponds to the inquency of light absorbed. This frequency generally lies in the visible region. The colour observed corresponds to the implementary colour of the light absorbed. The frequency of the limit absorbed is determined by the nature of the ligand. In aqueous aintions where water molecules are the ligands, the colour of the limit observed are listed in table.

Note: Formation of coloured compound is due to excitation of the form  $d \in to dy$  or  $t_{2g}$  to  $e_g$  orbital).

It take of complex ions, d-orbitals are split into two different sets the to crystal field effect, one consisting of lower energy orbitals  $d \in \mathbb{R}$  and the other consisting of higher energy orbitals  $(d\gamma)$ . In  $[H,D]_{\mathbb{R}}^{2^{-1}}$ ,  $[H,D]_{\mathbb{R}}^{2^{-1}}$ , [H,D]

$$\mathcal{E}_{z}$$
 or  $d$ ?

 $\mathcal{E}_{z}$  or  $d \in \mathbb{N}$ 

Ground state

In the allow wavelength, the electron is excited to



Since yellow wavelength is absorbed from visible region of light, the blue and red light will be transmitted and solution of  $[\mathrm{Ti}(\mathrm{H_2O})_6]^{3+}$  will appear purple which is the mixed effect of blue and red colours.

 $\mathrm{Sc}^{3+}$  and  $\mathrm{Ti}^{4+}$  have completely empty *d*-orbitals and are colourless.  $\mathrm{Cu}^{\oplus}$  and  $\mathrm{Zn}^{2+}$  have completely filled *d*-orbitals and there are no vacant *d*-orbitals for promotion of electrons, hence they are also colourless.

**Table 6.11** The colours of some of the first row transition metal ions (aquated)

Configuration	Example	Colour
$3d^0$	Sc <sup>3+</sup>	colourless
$3d^0$	Ti <sup>4+</sup>	colourless
$3d^1$	Ti <sup>3+</sup>	purple
$3d^1$	V <sup>4+</sup>	blue
$3d^2$	V <sup>3+</sup>	green
$3d^3$	V <sup>2+</sup>	violet
$3d^3$	Cr <sup>3+</sup>	violet
$3d^4$	Mn <sup>3+</sup>	violet
3d <sup>4</sup>	Cr <sup>2+</sup>	blue
$3d^5$	Mn <sup>2+</sup>	pink
$3d^5$	Fe <sup>3+</sup>	yellow
3 <i>d</i> <sup>6</sup>	Fe <sup>2+</sup>	green
$3d^7$	Co <sup>2+</sup>	pink
3 <i>d</i> <sup>8</sup>	Ni <sup>2+</sup>	green
3 <i>d</i> <sup>9</sup>	Cu <sup>2+</sup> blue	
$3d^{10}$	Zn <sup>2+</sup>	colourless

## 6.16 FORMATION OF COMPLEX COMPOUNDS

Complex compounds are formed by transition elements in contrast to such complexes are not formed by s- and p-blook elements.

The transition elements form complexes due to the following reason:

- 1. Comparatively smaller sizes of the metal ions
- 2. Their high charges
- 3. They have high charge density (i.e., charge/size ratio)
- **4.** Availability of vacant *d*-orbitals for bond formation

#### **6.17 CATALYTIC PROPERTIES**

The transition metals and their compounds are used as catalysts. There are various theories to explain their catalytic activity. Some of them are summarised as:

- 1. Variable oxidation theory: The catalytic activity may be due to their variable oxidation states (incomplete d-orbitals) and hence possess the capacity to absorb and re-emit wide range of energies. This makes the required energy of activation available.
- 2. Intermediate compound formation theory: According to this theory, the catalyst first forms an intermediate compound with one of the reactants, which then decomposes

or combines with another reactants to produce the product and the catalyst is regenerated. The catalyst in this process lowers free energy of activation and hence accelerates the rate of reaction.

**Note:** The catalyst only provides alternative path with lower energy of activation ( $E_{\rm act.}$ ). It does not change the equilibrium of the reaction.

For example, the oxidation of  $SO_2$  to  $SO_3$  in the presence of  $V_2O_5$  as catalyst takes place as follows:

i. 
$$SO_{2(g)}$$
 +  $V_2O_5$   $\longrightarrow$   $V_2O_4$  +  $SO_{3(g)}$   $\times$  2

Reactant Product  $\downarrow$  tetraoxide (Intermediate)

$$2V_2O_4$$
 +  $O_{2(g)}$   $\longrightarrow$   $2V_2O_5$  Intermediate ion Reactant  $\longrightarrow$   $2SO_{2(g)} + O_{2(g)}$   $\longrightarrow$   $2SO_{3(g)}$ 

ii. Fe<sup>3+</sup> catalyses the reaction between iodide (I<sup> $\odot$ </sup>) and persulphate or (peroxodisulphate) (S<sub>2</sub>O<sub>8</sub><sup>2-</sup>) ions to give I<sub>2</sub> and SO<sub>4</sub><sup>2-</sup> ions.

Net reaction: 
$$2I^{\Theta} + S_2O_8^{2-} \longrightarrow I_2 + 2SO_4^{2-}$$

Therefore from the above examples, it can be seen that how the change in oxidation state of transition metal accelerates the rate of the reaction through the formation of intermediate compound.

In example (i) vanadium (V) changes its O.S. from +5 to +4 and again to +5.

In example (ii), iron (Fe) changes its O.S. from +3 to +2 and to +3.

Thus it can be concluded that transition metal/ions become more effective as catalysts because they can change their oxidation states.

3. Adsorption theory: Due to high density of transition metal, they have large surface area in their finely divided state. The surface of the catalyst unlike the inner part of the bulk has free valencies which provide the seat for chemical forces of attraction.

Thus, catalysts at a solid surface involve the formation of bonds between reactant molecules and atoms of the surface of the catalyst (first series of transition metals utilise 3d and 4s electrons for bonding). As a result, the concentration of the reactants on the surface of catalyst increases. Moreover, bonds in the reacting molecules become weaker and thereby the energy of activation ( $E_{\rm act}$ ) is lowered. Hence the rate of reaction increases.

#### 6.17.1 CATALYSTS IN INDUSTRY

Some of the important catalytic processes are listed in table to give an idea about the utility of catalysts in industries.

Table 6.12 The utility of catalysts in industries

Process	Catalyst
1. Haber's process for the manufacture of ammonia $N_{2(g)} + 3H_{2(g)} \rightarrow 2NH_{3(g)}$	
2. Ostwald's process for the manufacture of nitric acid $4NH_{3(g)} + 5O_{2(g)} $ $\rightarrow 4NO_{(g)} + 6H_2O_{(g)}$ $2NO_{(g)} + O_{2(g)} \rightarrow 2NO_{(g)}$ $4NO_{2(g)} + 2H_2O_{(f)} + O_{2(g)}$ $\rightarrow 4HNO_{3(aq)}$	Platinised asbestos: temperature 573 K.
3. Contact process for the manufacture of sulphuric acid $2SO_{2(g)} + O_{2(g)} \rightarrow 2SO_{3(g)}$ $SO_{3(g)} + H_2SO_{4(aq)} \rightarrow H_2S_2O_{7(aq)}$ Oleum $H_2S_2O_{7(l)} + H_2O_{(l)} + O_{2(g)} \rightarrow 2H_2O_{4(aq)}$	Platinised asbestors or vanadium pentoxide (V <sub>2</sub> O <sub>5</sub> ) temperature 673–723K.

# 6.18 FORMATION OF NON-STOICHIOMETRIC COMPOUNDS AND INTERSTITIAL COMPOUNDS

#### Formation of interstitial compounds:

1. Interstitial compounds are those which are formed when small atoms like H, N, C or B are trapped inside the crystal lattices of metals. They are usually non-stoichiometric and are neither typically ionic nor covalent.

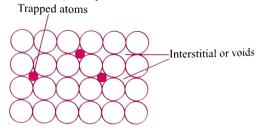


Fig. 6.7 Formation of interstitial compounds

- 2. These small atoms enter into the void sites between the packed atoms of the crystalline metal, e.g., TiC, Mn<sub>4</sub>N, Fe<sub>3</sub>H, TiH<sub>2</sub>, etc. The formulae quoted do not, of course, correspond to any normal oxidation state of the metal and often non-stoichiometric material is obtained with such composition as VH<sub>0.56</sub> and TiH<sub>1.7</sub>, Fe<sub>0.98</sub>O, Fe<sub>0.86</sub>S.
- 3. Because of the nature of their composition, these compounds are referred to as interstitial compounds. The principal

physical and chemical characteristics of these compounds place as follows:

They have high melting points, higher than those of pure metals.

They are very hard, some borides approach diamond in hardness.

They retain metallic conductivity.

They are chemically inert.

## 6.19 ALLOY FORMATION

1. An alloy is a blend of metals prepared by mixing the components. Alloys may be homogeneous solid solutions in which the atoms of one metal are distributed randomly among the atoms of the other. Such alloys are formed by atoms with metallic radii that are within about 15% of each other.

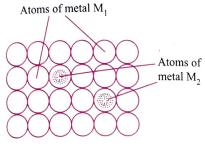


Fig. 6.8 Formation of alloys

- Because of similar radii and other characteristics of transition metals, alloys are readily formed by these metals. The alloys so formed are hard and have often high melting points. But the melting point of alloys is less than their individual metals.
- 3. The best known examples are ferrous alloys; chromium, vanadium, tungsten, molybdenum and manganese are used for the production of variety of steels and stainless steel.

#### ILLUSTRATION 6.13

What is meant by 'disproportionation' of an oxidation state? Give an example.

When a particular oxidation state becomes less stable relative to other oxidation states, one lower, one higher, it is said to undergo disproportionation. For example, manganese(VI) becomes unstable relative to manganese(VII) and manganese(IV) in acidic solution.

$$3Mn^{VI}O_4^{2-} + 4H^{\oplus} \longrightarrow 2Mn^{VII}O_4^{\Theta} + Mn^{IV}O_2 + 2H_2O$$

## 6.20 OXIDES AND OXOANIONS OF TRANSITION METALS

- 1. The oxides of 3d series are generally formed from the reaction of metals with  $O_2$  at high temperature. The oxides are formed in the oxidation states +1 to +7.
- 2. All the metals except scandium (Sc) form the oxide with the formula MO which are ionic in nature. As the oxidation number of the metal increases, ionic character decreases, e.g., Mn<sub>2</sub>O<sub>7</sub> is a covalent green oil. Even CrO<sub>3</sub> and V<sub>2</sub>O<sub>5</sub> have low melting points.

$$+2$$
  $+8/3$   $+3$   $+4$   $+7$   $MnO > Mn3O4 > Mn2O3 > MnO2 > Mn2O7$ 

#### Ionic character decreases

3. In general, the oxides in the lower oxidation states of the metals are basic and in their higher oxidation states, they are acidic whereas in the intermediate oxidation state, the oxides are amphoteric.

For example, the behaviour of the oxides of manganese may be represented as follows:

Thus,  $Mn_2O_7$  dissolves in water to give the acid  $HMnO_4$ . In case of vanadium, there is a gradual change from the basic  $V_2O_3$  to less basic  $V_2O_4$  and to amphoteric  $V_2O_5$  though it is mainly acidic. Thus,  $V_2O_4$  dissolves in acids to give  $VO^{2^+}$  salts whereas  $V_2O_5$  reacts with alkalies as well as acids to give  $VO_4^{3^-}$  and  $VO_4^{\oplus}$  respectively.

Similarly, CrO is basic, Cr<sub>2</sub>O<sub>3</sub> is amphoteric while CrO<sub>3</sub> is acidic, having +2, +3 and +6 OS respectively.

Thus,  $CrO_3$  dissolves in water to give the acids  $H_2CrO_4$  and  $H_2Cr_2O_7$ .

- **4.** Oxides are insoluble in water. However, basic and amphoteric oxides dissolve in non-oxidising acids like HCl to form hydrated ions  $[M(H_2O)_6]^{n+}$ . Some of the oxides dissolve in acids and bases to form oxometallic salts. such as  $CrO_4^{\ 2-}$ ,  $Cr_2O_7^{\ 2-}$  and  $MnO_4^{\ \Theta}$ .
  - i. They are highly coloured (generally black).
  - ii. Polymeric in structure rather than purely ionic.
- 5. Oxides of first two transition metals:
  - $\begin{aligned} \textbf{i.} \quad & \textbf{Basic oxides: } Sc_2O_3, TiO, Ti_2O_3, VO, V_2O_3, MnO, \\ & FeO, Fe_2O_3, Fe_3O_4, CoO, NiO, Cu_2O \end{aligned}$
  - ii. Acidic oxides:  $V_2O_5$ ,  $CrO_3$ ,  $Mn_2O_7$
  - iii. Amphoteric oxides: TiO<sub>2</sub>, VO<sub>3</sub>, Cr<sub>2</sub>O<sub>3</sub>, CrO<sub>2</sub>, Mn<sub>2</sub>O<sub>3</sub>, Mn<sub>3</sub>O<sub>4</sub>, MnO<sub>2</sub>, CuO

**Note:** Some other types of oxides like mixed oxides, non-stoiochiometric oxides and spinels are also formed by transition metals.  $CoMoO_4$  and  $ZnFe_2O_4$  are simple mixed oxides. Some mixed oxides contain same metal ion in two different oxidation states, e.g.,  $Fe_3O_4$  contains two oxides (FeO and  $Fe_2O_3$ ) in which Fe has +2 and +3 oxidation states respectively.  $Mn_2O_3$  is also a mixed oxides of MnO and  $MnO_2$ .

The oxides of iron such as  $Fe_{0.91}O$  and  $Fe_{0.95}O$  are non-stoichiometric oxides as in these oxides iron metal ratio is not in whole number.

Spinels are special types of oxides in which oxygen atoms have face centred cubic (fcc) lattice. For example,

 $ZnFe_2O_4$  is a normal spinel in which the trivalent (Fe<sup>3+</sup>) ions occupy the octahedral sites while divalent ( $Zn^{2+}$ ) ions occupy the tetrahedral sites. The spinel  $Fe(Fe_2)O_4$  is an inverse spinel as in it the trivalent ( $Fe^{3+}$ ) ions occupy the tetrahedral sites.

## 6.22 Inorganic Chemistry 6.21 COMPARISON OF THE FIRST TWO TRANSITION METALS THROUGH THE

0.2	FLECTRON	CONFIGURATION		$d^3$
	d-ELECTRON	CONFIGURATION	$d^2$	
	$d^{0}$ Se <sup>3+</sup> , Ti <sup>4+</sup> , V <sup>5+</sup> , Cr <sup>6+</sup> and Mn <sup>7+</sup> But Fe <sup>8+</sup> is unknown	$d^1$ Except V <sup>4+</sup> others with $d^1$ configuration are either reducing or disproportionates.	$Ti^{2^+}$ to $Fe^{6^+}$ , $V^{3^+}$ and $Ti^{2^+} \Rightarrow$ is reducing $Fe^{6^+} \Rightarrow$ is strongly oxidising $V^{3^+} \Rightarrow$ is also reducing	Only Cr <sup>3+</sup> is stable and forms complexes
		$3CrO_{4}^{3-} + 8H^{\oplus} \rightarrow 2CrO_{4}^{2-} + Cr^{3+} + 4H_{2}O$ $3MnO_{4}^{2-} + 4H^{\oplus} \rightarrow 2MnO_{4}^{\ominus} + MnO_{2} + 2H_{2}O$	d <sup>6</sup>	d <sup>7</sup>
	d <sup>4</sup> Really no stable species  Strongly reducing  Cr <sup>2+</sup> ⇒ Strongly reducing  Mn <sup>3+</sup> ⇒ Disproportionates	Fe <sup>3+</sup> is reduced to Fe <sup>2+</sup>	$E_0^{2+} \rightarrow Stable$ and mild reducing	is oxidised in presence of
	d <sup>8</sup>	d <sup>9</sup>		
	Ni <sup>2+</sup> is the most important	This comiguration is found in	$Cu^{\oplus}$ and $Zn^{2+}$ are important $Zi^{2+}$ is the only state known for zinc $Cu^{\oplus}$ is readily oxidised to $Cu^{2+}$	

### 6.21.1 GENERAL GROUP TRENDS IN THE CHEMISTRY OF d-BLOCK METALS

	Group: 3		Group: 4		Group: 5
	Scandium (Sc) (21) Yttrium (Y) (39) Lanthanum (La) (57)		Titanium (Ti) (22) Zirconium (Zr) (40) Hafnium (Hf) (72)		Vanadium (V) (23) Niobium (Nb) (41) Tantalum (Ta) (73)
	They are studied along with lanthanoids	i.	They are lustrous, silvery white metals with high m. pt.	i.	Shining silvery metals
		ii.	Electropositive but less than group 3	ii.	Less electropositive than groups 4 and
		iii.	On heating reacts with most non-metals ( $O_2$ and $H_2$ ) and Ti reacts with $N_2$	iii.	Size of Nb ≈ Ta (Due to consequence lanthanoid contraction). Shows simil properties
		iv.	No effect of cold acid ( except HF)	iv.	Shows all O.S. from +1 to +5
		v.	Stable O.S. is +4	v.	V <sup>4+</sup> is most stable
		vi.	Lower O.S. for Zr and Hf not known	vi.	Nb <sup>5+</sup> and Ta <sup>5+</sup> are most stable.
		vii.	Compounds are: TiCl <sub>4</sub> , ZrCl <sub>4</sub> , HfCl <sub>4</sub> TiO <sub>2</sub> , ZrO <sub>2</sub> , HfO <sub>2</sub>	vii.	V shows all O.S. from +5 to +2
		viii.	Zr and Hf (160 and 159 pm) of almost same size show similar properties	viii.	V is used to increase the strength at toughness of steel
	Group: 6		Group: 7		0
N	Chromium (Cr) (24) Molybdenum (Mo) (42) ungsten (W) (74)		Manganese (Mn) (25) Technetinum (Tc) (43) Rhenium (Re) (75)		Group: 8  Iron (Fe) (26) Ruthenium (Ru) (44) Osmium (Os) (76)
. Si	ilvery, lustrous, soft (when pure)	i.	They are obtained from fission waste	i.	Ru and Os are stable to atmospheri
		••	D.		attack
Sh	nows +6 O.S. in oxo anions	ii.	Re is rare, resembles Tc in properties	ii.	Ru and Os show +8 O.S.

Mo and W, strong M-M bonding	iv.	Important O.S. of Mn are +2 and +4.	iv.	Fe show +2 and + 3 O.S.
In Mo and W, strong M-M bonding  Cr is used in lather industry and for making, stainless steel and chrome	v.	Mn is used in all steels	v.	Fe is used in steel
plating plating Mo is used in X-ray tubes Compounds of Mo and W are used as catalysts	vi.	Re is used in electronic filaments, high temp. thermocouples and flash bulbs		
Group: 9		Group: 10		Group: 11
Cobalt (Co) (27) Rhodium (Rh) (45) Iridium (Ir) (77)	i ledell	Nickel (Ni) (28) Palladium (Pd) (46) Platinum (Pt) (78)		Copper (Cu) (29) Silver (Ag) (47) Gold (Au) (79)
Co shows +2 and +3 O.S.	i.	Unreactive at normal temperature	i.	Reactivity decreases down the group
But +3 O.S. in aq. soln. is a strong		Ni and Pd reacts with halogens on heating	ii.	Au is inert and resembles Pt. in reactivity
It can oxidise even H <sub>2</sub> O with evolution of H <sub>2</sub>	iii.	Reactivity decreases from Ni to Pd and to Pt	iii.	Cu shows +2, Ag shows +1 and Au show +3 O.S. in aq. soln.
Rh and Ir show +3 O.S.	iv.	Ni and Pd show +2 O.S.	iv.	1E <sub>1</sub> for Ag is lowest
Ir shows occasionally +4 O.S.	v.	Pt shows +2 and +4 O.S.	v.	$1E_1 + 1E_2 + 1E_3$ is lowest for Au
Co <sup>3+</sup> form complexes with N-donor ligands	vi.	Ni is used as alloy Nichrorne (60% Ni + 40% Cr) German silver (Cu 25–30%), (Zn 25–30%) (Ni 40–50%)	vi.	They are not related in their chemica behaviour
Co-compounds are used in ceramics, paint and as catalyst	vii.	Pt and Pd are used as catalyst		
Group: 12				
Zinc (Zn) (30), Cadmium (Cd) (48) Mercury (Hg) (80)				
Zn and Cd are similar in their reactivity Hg shows different reactivity				8 · · · · · · · · · · · · · · · · · · ·
All have $d^{10}$ configuration				
Hg <sup>⊕</sup> exists as Hg <sub>2</sub> <sup>2+</sup>		and a second		
Because of filled $d^{10}$ configuration. They show few properties of transition				

# 6.22 SOME IMPORTANT COMPOUNDS OF TRANSITION ELEMENTS CONTAINING OXOANIONS

### 6.22.1 POTASSIUM DICHROMATE (K2Cr2O7)

elements

Preparation: It is prepared from the ore called chromite or fetrochrome or chrome iron, FeO·Cr<sub>2</sub>O<sub>3</sub> or FeCr<sub>2</sub>O<sub>4</sub> by the following steps.

1. Preparation of sodium chromate: The ore is finely powdered, mixed with sodium carbonate and quick lime and then roasted, i.e., heated to redness in a reverberatory furnace with free exposure to air when sodium chromate (yellow in

**colour)** is formed and carbonate dioxide is evolved. Quick lime keeps the mass porous and thus facilitates oxidation. 
$$4\text{FeO}\cdot\text{Cr}_2\text{O}_3 + \text{O}_2 \longrightarrow 2\text{Fe}_2\text{O}_3 + 4\text{Cr}_2\text{O}_3$$
  $2\text{Na}_2\text{CO}_3 + 2\text{Cr}_2\text{O}_3 + 3\text{O}_2 \longrightarrow 4\text{Na}_2\text{CrO}_4 + 4\text{CO}_2] \times 2$   $4\text{FeO}\cdot\text{Cr}_2\text{O}_3 + 8\text{Na}_2\text{CO}_3 + 7\text{O}_2$  Chromite ore 
$$\longrightarrow 8\text{Na}_2\text{CrO}_4 + 2\text{Fe}_2\text{O}_3 + 8\text{CO}_2$$
 Sodium chromate (Yellow)

The fused mass is extracted with water and filtered.

2. Conversion of sodium chromate into sodium dichromate:

The filtrate containing sodium chromate solution is treated with conc. H<sub>2</sub>SO<sub>4</sub> when Na<sub>2</sub>CrO<sub>4</sub> is converted into Na<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>·2H<sub>2</sub>O

$$2\text{Na}_2\text{CrO}_4 + \text{H}_2\text{SO}_4 \longrightarrow \text{Na}_2\text{Cr}_2\text{O}_7 + \text{Na}_2\text{SO}_4 + \text{H}_2\text{O}$$
Sodium dichromate
(orange)

Na<sub>2</sub>SO<sub>4</sub> being less soluble crystallises out as decahydrate, Na<sub>2</sub>SO<sub>4</sub>·10H<sub>2</sub>O and is removed.

#### 3. Conversion of Na, Cr, O<sub>7</sub> into K, Cr, O<sub>7</sub> (orange red):

Na<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> is more soluble than K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>. The latter is then prepared by treating the solution of Na<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> with KCl.

$$2Na_2Cr_2O_7 + 2KCl \longrightarrow K_2Cr_2O_7 + 2NaCl$$
Sodium Potassium dichromate dichromate (orange red)

#### **Properties:**

- 1. K<sub>2</sub>Cr<sub>2</sub>O<sub>2</sub> is orange red crystal, melting point 669 K, moderately soluble in cold water but freely soluble in hot water.
- 2. The chromates and dichromates are interconvertible in aqueous solution and Cr<sub>2</sub>O<sub>2</sub><sup>2-</sup> ions are invariably in equilibrium with  $CrO_4^{2-}$  ions at pH = 4, i.e.

$$\begin{array}{c} \operatorname{Cr}_2\operatorname{O_7}^{2-} + 2\operatorname{OH}^{\scriptsize \bigcirc} & \longrightarrow 2\operatorname{Cr}\operatorname{O_4}^{2-} + 2\operatorname{H}_2\operatorname{O} \\ \operatorname{Orange\ red} & \operatorname{Yellow} \\ \\ 2\operatorname{Cr}\operatorname{O_4}^{2-} + 2\operatorname{H}^{\scriptsize \oplus} & \longrightarrow \operatorname{Cr}_2\operatorname{O_7}^{2-} + \operatorname{H}_2\operatorname{O} \\ \operatorname{Yellow} & \operatorname{Orange\ red} \\ \\ \operatorname{Cr}\operatorname{O_4}^{2-} & \xrightarrow{\scriptsize \bigcirc} \operatorname{Cr}_2\operatorname{O_7}^{2-} \\ \operatorname{Yellow} & \operatorname{Orange\ red} \\ \end{array}$$

On adding an alkali (i.e., increasing the pH of solution), the H<sup>⊕</sup> ions are used up and according to the law of chemical equilibrium, the reaction proceeds in the forward direction producing yellow chromate solution. On the other hand, when an acid is added (i.e., pH of the solution is decreased). the concentration of H<sup>®</sup> ions is increased and the reaction proceeds in the backward direction producing an orange red dichromate solution.

The oxidation state of chromium in chromate and dichromate is same, i.e., +6.

#### 3. Action of concentrated sulphuric acid:

a. In cold, red crystals of chromic anhydride (chromium trioxide) are formed.

$$K_2Cr_2O_7 + 2H_2SO_4 \longrightarrow 2CrO_3 + 2KHSO_4 + H_2O_3$$

b. On heating the mixture, oxygen is evolved.

$$2K_2Cr_2O_7 + 8H_2SO_4 \longrightarrow 2K_2SO_4 + 2Cr_2(SO_4)_3 + 8H_2O + 3O_2$$

4. Oxidising properties: Potassium dichromate is a powerful oxidising agent. In acidic solution, its oxidising action can be represented as follows:

Ionic equation:

$$Cr_2O_7^{2-} + 14H^{\oplus} + 6e^{\Theta} \longrightarrow 2Cr^{3+} + 7H_2O$$
  
[ $E^{\Theta} = +1.31$ ] (*n* factor = 6)

Molecular equation:

$$2K_2Cr_2O_7 + 4H_2SO_4 \longrightarrow K_2SO_4 + Cr_2(SO_4)_3 + 3[O]$$

Thus, Ew of 
$$K_2Cr_2O_7$$
  
=  $\frac{Mw \text{ of } K_2Cr_2O_7}{6} = \frac{294}{6} = 49$ 

Thus, Ew of  $K_2Cr_2O_7$   $= \frac{Mw \text{ of } K_2Cr_2O_7}{6} = \frac{294}{6} = 49$ The full ionic equation is obtained by adding the half.

Cr  $O^{2-}$  ion in acidic medium to the half. reaction for  $\operatorname{Cr_2O_7}^{2-}$  ion in acidic medium to the half reaction for the reducing agent, balancing  $w_{\text{here}_{\nu_{e_i}}}$ 

**a.** It oxidises iodides to iodine  $(2I^{\Theta} \longrightarrow I_2 + 2e^{\Theta})$ 

$$\operatorname{Cr_2O_7}^{2-} + 14\operatorname{H}^{\oplus} + 6\operatorname{I}^{\ominus} \longrightarrow 2\operatorname{Cr}^{3+} + 7\operatorname{H_2O} + 3\operatorname{I_2}$$
Orange red

Green

(n factors

This reaction is used in the estimation of iodide  $ion_{S_1}$ volumetric analysis.

**b.** It oxidises ferrous salts to ferric salts:  $(Fe^{2+} \longrightarrow Fe^{2})$  $Cr_2O_7^{2-} + 14H^{\oplus} + 6Fe^{2+} \longrightarrow 2Cr^{3+} + 6Fe^{3+} + 7H_0$ This reaction is used in the estimation of ferrous ion

in the volumetric analysis. c. It oxidises  $H_2S$  to  $S: (S^{2-} \longrightarrow S)$ 

 $Cr_2O_7^{2-} + 8H^{\oplus} + 6H_2S \longrightarrow 2Cr^{3+} + 7H_2O + 3S$ 

d. It oxidises sulphur dioxide to sulphate ion:

$$(SO_2 \longrightarrow SO_4^{2-}) (n \text{ factor} = 2)$$

$$Cr_2O_7^{2-} + 3SO_2 + 2H^{\oplus} \longrightarrow 2Cr^{3+} + H_2O + 3SO_4^{2-}$$

The reaction is used in the preparation of chrome alum e. It oxidises sulphites (SO<sub>3</sub><sup>2-</sup>) to sulphate (SO<sub>2</sub><sup>2-</sup>):

$$Cr_2O_7^{2-} + 8H^{\oplus} + 3SO_3^{2-} \longrightarrow 2Cr^{3+} + 3SO_4^{2-} + 4H$$

**f.** It disproportionate thiosulphate  $(S_2O_3^{2-})$  to sulphate  $(SO_4^{2-})$ 

and S: 
$$(S_2O_3^{2-} \longrightarrow SO_4^{2-})$$
 (*n* factor = 2)  
 $Cr_2O_7^{2-} + 14H^{\oplus} + 6e^{\ominus} \longrightarrow 2Cr^{3+} + 7H_2O$   
 $S_2O_3^{2-} + H_2O \longrightarrow SO_4^{2-} + S + 2e^{\ominus} + 2H^{\oplus}] \times 3$   
 $Cr_2O_7^{2-} + 8H^{\oplus} + 3S_2O_3^{2-} \longrightarrow 2Cr^{3+} + 3SO_4^{2-} + 3S + 4H_2O$ 

**g.** It oxidises nitrites  $(NO_2^{\Theta})$  to  $NO_3^{\Theta}$  (nitrates)

$$(NO_2^{\Theta} \longrightarrow NO_3^{\Theta}) (n \text{ factor} = 2)$$

$$Cr_2O_7^{2-} + 8H^{\oplus} + 3NO_2^{\Theta} \longrightarrow 2Cr^{3+} + 3NO_3^{\Theta} + 4H_2^{\Theta}$$

h. It oxidises halogen acids (HX) to halogens

$$(2Cl^{\Theta} \longrightarrow Cl_{2}) (n \text{ factor} = 2)$$

$$Cr_{2}O_{7}^{2-} + 6Cl^{\Theta} + 14H^{\Theta} \longrightarrow 2Cr^{3+} + 3Cl_{2} + 7H_{2}O_{3}^{2-}$$

i. It oxidises stannous salts  $(Sn^{2+})$  to stannic salts  $(Sn^{4+})$  $(\operatorname{Sn}^{2+} \longrightarrow \operatorname{Sn}^{4+}) (n \operatorname{factor}^{=2})$ 

$$Cr_2O_7^{2-} + 14H^{\oplus} + 3Sn^{2+} \longrightarrow 2Cr^{3+} + 3Sn^{4+} + 7H_2^0$$

**j.** It oxidises arsenites  $(AsO_3^{3-})$  to arsenates  $(AsO_4^{3-})$ 

(AsO<sub>3</sub><sup>3-</sup> 
$$\longrightarrow$$
 AsO<sub>4</sub><sup>3-</sup>) ( $n \text{ factor}^{=2}$ )  
 $\text{Cr}_2\text{O}_7^{2-} + 14\text{H}^{\oplus} + 6e^{\Theta} \longrightarrow 2\text{Cr}^{3+} + 7\text{H}_2\text{O}$   
AsO<sub>3</sub><sup>3-</sup>  $+ \text{H}_2\text{O} \longrightarrow \text{AsO}_4^{3-} + 2e^{\Theta} + 2\text{H}^{\oplus}$ ]  $\times$  3

$$\frac{\text{Cr}_2\text{O}_7^{2-} + 8\text{H}^{\oplus} + 3\text{AsO}_3^{3-} \longrightarrow 2\text{Cr}^{3+} + 3\text{AsO}_4^{3-} + 4\text{H}_2^{0}}{\text{Cr}_2\text{O}_7^{2-} + 8\text{H}^{\oplus} + 3\text{AsO}_3^{3-} \longrightarrow 2\text{Cr}^{3+} + 3\text{AsO}_4^{3-} + 4\text{H}_2^{0}}$$

$$(C_2O_4^{2-} \longrightarrow 2CO_2) \text{ (n factor = 2)}$$

$$Cr_2O_7^{2-} + 14H^{\oplus} + 6e^{\Theta} \longrightarrow 2Cr^{3+} + 7H_2O$$

$$C_2O_4^{2-} \longrightarrow 2CO_2 + 2e^{\Theta} ] \times 3$$

$$\underbrace{\text{Cr,O}_{7}^{2-} + 14\text{H}^{\oplus} + 3\text{C}_{2}\text{O}_{4}^{2-} \longrightarrow 2\text{Cr}^{3+} + 6\text{CO}_{2} + 7\text{H}_{2}\text{O}}_{2}}$$

l. It oxidises ethyl alcohol (C<sub>2</sub>H<sub>5</sub>OH) to acetaldehyde (or ethanal) (CH<sub>3</sub>CHO).

$$(C_2H_5OH \longrightarrow CH_3CHO)$$
 (*n* factor = 2)  
 $K_2Cr_2O_7 + 4H_2SO_4 \longrightarrow K_2SO_4 + Cr_2(SO_4)_3 + 4H_2O + 3O_4$   
 $CH_3CH_3OH + O \longrightarrow CH_3CHO + H_2O ] \times 3$ 

$$K_2Cr_2O_7 + 4H_2SO_4 + 3C_2H_5OH \longrightarrow K_2SO_4 +$$
 $Cr_2(SO_4)_3 + 3CH_3CHO + H_2O$ 

#### lonic equation:

$$\begin{array}{ccc} \operatorname{Cq_2O_7^{2-}} + 14 \operatorname{H}^{\oplus} + 6 e^{\Theta} & \longrightarrow 2 \operatorname{Cr}^{3+} + 7 \operatorname{H}_2 \operatorname{O} \\ \operatorname{C}_2 \operatorname{H}_5 \operatorname{OH} & \longrightarrow \operatorname{CH}_3 \operatorname{CHO} + 2 e^{\Theta} + 2 \operatorname{H}^{\oplus} \end{array} ] \times 3 \\ (2x = -4) & (2x = -2) \end{array}$$

$$Cr_2O_7^{2-} + 8H^{\oplus} + 3C_2H_5OH \longrightarrow 2Cr^{3+} + 3CH_3CHO + 7H_2O$$

m. It oxidises acetaldehyde or ethanal (CH<sub>3</sub>CHO) to acetic acid or ethanoic acid (CH<sub>3</sub>COOH).

$$(CH_3CHO \longrightarrow CH_3COOH) (n \text{ factor} = 2)$$

$$K_2Cr_2O_7 + 4H_2SO_4 \longrightarrow K_2SO_4 + Cr_2(SO_4)_3 + 4H_2O + 3O$$

$$CH_3CHO + O \longrightarrow CH_3COOH] \times 3$$

$$K_2Cr_2O_7 + 4H_2SO_4 + 3CH_3CHO \longrightarrow K_2SO_4 + Cr_2(SO_4)_3 + 4H_2O + 3CH_3COOH$$

#### Ionic equation:

Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup> + 14H<sup>$$\oplus$$</sup> + 6e <sup>$\ominus$</sup>   $\longrightarrow$  2Cr<sup>3+</sup> + 7H<sub>2</sub>O  
H<sub>2</sub>O + CH<sub>3</sub>CHO  $\longrightarrow$  CH<sub>3</sub>COOH + 2e <sup>$\ominus$</sup>  + 2H <sup>$\oplus$</sup> ] × 3  
(2x = -2) (2x = 0)

$$Cr_2O_7^{2-} + 8H^{\oplus} + 3CH_3CHO \longrightarrow 2Cr^{3+} + 3CH_3COOH + 4H_2O$$

#### <sup>n.</sup> Reaction with $H_2O_2$ :

i. In this case H<sub>2</sub>O<sub>2</sub> oxidises ice-cold acidified K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> solution containing ether to CrO<sub>5</sub> (chromium diperoxide or chromic peroxide or blue perchromic acid). The ethereal layer turns intense blue in colour due to formation of CrO<sub>5</sub> or [CrO·(O<sub>2</sub>)<sub>2</sub>]. The blue colour fades away gradually due to the decomposition of CrO<sub>5</sub> into Cr<sup>3+</sup> ions and O<sub>2</sub>. The structure of CrO<sub>5</sub> is called butterfly structure and is shown as

$$0$$
 $Cr$ 
 $0$ 

$$\begin{array}{c} \text{K}_2\text{Cr}_2\text{O}_7 + \text{H}_2\text{SO}_4 + 4\text{H}_2\text{O}_2 \xrightarrow{\text{Ether}} 2\text{CrO}_5 + \text{K}_2\text{SO}_4 + 5\text{H}_2\text{O} \\ \text{Dilute} & \text{Deep blue} & \dots \dots \text{(i)} \end{array}$$

#### Ionic equation (It is uncertain equation):

$$3H_2O + Cr_2O_7^{2-} \longrightarrow 2CrO_5 + 8e^{\Theta} + 6H^{\oplus}$$

$$(2x = 12) \qquad (2x = 20)$$

$$H_2O_2 + 2H^{\oplus} + 2e^{\Theta} \longrightarrow 2H_2O ] \times 4$$

$$Cr_2O_7^{2-} + 4H_2O_2 + 2H^{\oplus} \longrightarrow 2CrO_5 + 5H_2O \qquad ...... (ii)$$

ii. Similar reaction of H<sub>2</sub>O<sub>2</sub> under similar conditions is also shown by K<sub>2</sub>CrO<sub>4</sub> (potassium chromate).

$$\begin{array}{c} \text{K}_2\text{CrO}_4 + \text{H}_2\text{SO}_4 + 2\text{H}_2\text{O}_2 \xrightarrow{\text{Ether}} \text{CrO}_5 + \text{K}_2\text{SO}_4 + 3\text{H}_2\text{O} \\ \text{Dilute} & \text{Deep blue} & \dots \dots & \text{(iii)} \end{array}$$

#### Ionic equation (It is uncertain equation):

$$H_{2}O + CrO_{4}^{2-} \longrightarrow CrO_{5} + 4e^{\Theta} + 2H^{\Theta}$$

$$(x = 6) \qquad (x = 10)$$

$$H_{2}O_{2} + 2H^{\Theta} + 2e^{\Theta} \longrightarrow 2H_{2}O ] \times 2$$

$$CrO_{4}^{2-} + 2H^{\Theta} + 2H_{2}O_{2} \longrightarrow CrO_{5} + 3H_{2}O \qquad ....... (iv)$$

#### Note:

- 1. The molecular equations of H<sub>2</sub>O<sub>2</sub> with Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup> and CrO<sub>4</sub><sup>2-</sup> are shown in above in Eqs. (i) and (iii) respectively. In CrO<sub>5</sub>, O.S. of Cr = +6. But considering O.S. of Cr = +10 (which is not possible), their ionic equations are shown above in Eqs. (ii) and (iv) respectively.
- 2. Surprisingly the result of molecular and ionic equations (i), (ii), (iii) and (iv) are same. Therefore, ionic equations (ii) and (iv) are valid.

Chromyl chloride test (Reaction with a chloride and conc. sulphuric acid). When heated with conc. HCl or with a chloride and strong H<sub>2</sub>SO<sub>4</sub>, reddish brown vapours of chromyl chloride are obtained.

$$K_2Cr_2O_7 + 2H_2SO_4 \longrightarrow 2KHSO_4 + 2CrO_3 + H_2O$$

$$KCl + H_2SO_4 \longrightarrow KHSO_4 + HCl] \times 4$$

$$2CrO_3 + 4HCl \longrightarrow 2CrO_2Cl_2 + 2H_2O$$

$$K_2Cr_2O_7 + 4KCl + 6H_2SO_4 \longrightarrow 2CrO_2Cl_2 + 6KHSO_4 + 3H_2O_4$$

This reaction is used in the detection of  $Cl^{\Theta}$  ions in qualitative analysis.

Note: Chlorides of Ag, Hg, Pb and Sn do not give this test.

#### Uses

 In volumetric analysis, it is used as a primary standard for the estimation of Fe<sup>2+</sup> (ferrous ions) and I<sup>⊕</sup> (iodides) in redox titrations.

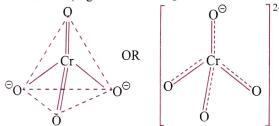
**Note:** Na<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> is not used in volumetric analysis because it is deliquescent.

- 2. It is used in the industry.
  - a. In the preparation of chrome alum  $\begin{array}{l} K_2SO_4.Cr_2(SO_4)_3\cdot 24H_2O \ \ and \ \ other \ \ industrially \\ important \ compounds \ such \ as \ Cr_2O_3 \ , \ CrO_3, \ CrO_2O_2, \\ K_2CrO_4, \ CrCl_3 \ \ etc. \end{array}$

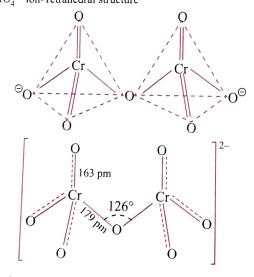
- c. In chrome tanning in leather industry.
- d. In photography and in hardening gelatine film.
- 3. Both sodium and potassium dichromates are strong oxidizing agents. The sodium salt has a greater solubility in water and is extensively used as an oxidising agent in organic chemistry.

## 6.22.2 STRUCTURES OF $CrO_4^{2-}$ AND $Cr_2O_7^{2-}$ IONS

- 1. In Cr<sub>2</sub>O<sub>4</sub><sup>2-</sup> ion, Cr is sp<sup>3</sup> hybridised and all the Cr–O bonds are equivalent. In Cr<sub>2</sub>O<sub>4</sub><sup>2-</sup> ion, the two Cr–O bonds which share an oxygen atom at the common vertex of two tetrahedral units are longer than the other six equivalent Cr–O bonds
- 2. In  $\text{CrO}_4^{2^-}$  and  $\text{Cr}_2\text{O}_7^{2^-}$  ions, Cr(VI) has  $d^0$  configuration. Hence, yellow colour of  $\text{CrO}_4^{2^-}$  and orange colour of  $\text{Cr}_2\text{O}_7^{2^-}$  are not due to d-d transition but due to charge transfer, i.e., momentary transfer of charge from O-atom to metal atom thereby changing  $\text{O}^{2^-}$  ion momentarily to  $\text{O}^{\odot}$  ion and reducing the oxidation state of Cr from + 6 to + 5. LMCT (Ligand metal charge transfer)



a. CrO<sub>4</sub><sup>2-</sup> ion-Tetrahedral structure



**b.**  $\operatorname{Cr_2O_7^{2-}}$  ion-Two tetrahedra sharing one oxygen atom at one corner

Fig. 6.9 (a) Structure of  $Cr_{2}^{0}$  ion (b) Structure of  $Cr_{2}^{0}$  ion

## 6.23 POTASSIUM PERMANGANATE (KMnO<sub>4</sub>)

#### Preparation:

 KMnO<sub>4</sub> is prepared by fusion of the mineral, pyrolusite, MnO<sub>2</sub> (blackish brown) with an alkali metal hydroxide (e.g. KOH) in presence of air or oxidising agent such as KNO<sub>3</sub> or KClO<sub>3</sub>. This produces the dark green potassium manganale (K<sub>2</sub>MnO<sub>4</sub>).

 $\frac{2MnO_2}{2MnO_2} + \frac{4KOH + O_2}{Dark green} \rightarrow \frac{2K_2MnO_4 + 2H_2O}{Dark green}$ 

- Blackish blown

  2. K<sub>2</sub>MnO<sub>4</sub> disproportionates in a neutral or acidic solution give permanganate (MnO<sub>4</sub><sup>⊕</sup>).

  3MnO<sub>4</sub><sup>2-</sup> + 4H<sup>⊕</sup> → 2MnO<sub>4</sub><sup>⊕</sup> + MnO<sub>2</sub> + 2H<sub>2</sub>O

  Pink or purple
- Commercially it is prepared by the alkaline oxidative f<sub>USi0η</sub> of MnO<sub>2</sub> followed by the electrolytic oxidation of manganale (MnO<sub>4</sub><sup>2-</sup>) ion.

$$\begin{array}{c} \operatorname{MnO_2} \xrightarrow{\operatorname{Fused with KOH}} \operatorname{MnO_4}^{2^-} \\ \operatorname{oxidised with air} \\ \operatorname{or KNO_3} \\ \operatorname{At anode} \\ \operatorname{At anode} \\ \operatorname{Electrolytic oxidation in} \\ \operatorname{alkaline solution} \\ \operatorname{MnO_4}^{\ominus} + e^{\ominus} \\ \operatorname{Permanganate ion} \end{array}$$

**4.** In the laboratory  $\text{Mn}^{2+}$  (manganes) ion salt is oxidised by peroxodisulphate  $(S_2O_8^{2-})$  ion to  $\text{MnO}_4^{\odot}$  (permanganate ion.

Ionic equation:

$$4H_{2}O + Mn^{2+} \longrightarrow MnO_{4}^{\ominus} + 5e^{\ominus} + 8H^{\ominus}] \times 2$$

$$(x = 2) \qquad (x = 7)$$

$$2e^{\ominus} + S_{2}O_{8}^{2-} \longrightarrow 2SO_{4}^{2-}] \times 5$$

$$(2x - 16 = -2) \qquad (2x - 16 = -4)$$

$$2x = 14 \qquad 2x = 12$$

$$2Mn^{2+} + 5S_{2}O_{8}^{2-} + 8H_{2}O \longrightarrow 2MnO_{4}^{\ominus} + 10SO_{4}^{2-} + 16H^{\ominus}$$

#### **Properties:**

- 1. It exists as deep purple black prisms with greenish lustre. It is moderately soluble in water at room temperature. Its solubility increases with temperature. Its melting point is 523 K. It shows weak temperature- dependent paramagnetism. This can be explained by MOT (molecular orbital theory).
- 2. Action of heat: It undergoes decomposition, when heated at 750 K.

$$\begin{array}{lll} KMnO_4 & \xrightarrow{Heat} & K_2MnO_4 + MnO_2 + O_2 \\ \text{Purple} & \text{Dark green} & \text{Blackish brown} \\ K_2MnO_4 & \text{further decomposes to give potassium manganite} \\ K_2MnO_3. & \end{array}$$

 $K_2MnO_4 \longrightarrow 2K_2MnO_3 + O_2$ 3. Action of  $H_2SO_4$ :

$$2KMnO_4 + H_2SO_4 \text{ (cold conc.)} \longrightarrow Mn_2O_7 + KHSO_4 + H_2O_4 + Mn_2O_7 \xrightarrow{\Delta} 4MnO_2 + 3O_2$$

$$4KMnO_4 + 6H_2SO_4 \text{ (hot conc.)} \longrightarrow 2K_2SO_4 + 4MnSO_4 + 6H_2O_7 + 5O_2$$

$$\begin{array}{c}
\mathbf{OR} \\
4KMnO_4 + 3H_2SO_4 \longrightarrow K^{\oplus} + MnO_3^{\oplus} + 3HSO_4^{\Theta} + H_30^{\Theta}
\end{array}$$
Green

4. Action of heat in hydrogen gas:

$$2KMnO_4 \xrightarrow{\text{Heat}} 2KOH + 2MnO + 4H_2O$$

## 5, Oxidising properties:

In acidic medium (ionic equation):  

$$MnO_4^{\ominus} + 8H^{\oplus} + 5e^{\ominus} \longrightarrow Mn^{2+} + 4H_2O$$

(*n* factor = 5) 
$$(E^{\Theta} = +1.52 \text{ V})$$

$${}_{2KMnO_4} + 3H_2SO_4 \longrightarrow K_2SO_4 + 2MnSO_4 + 3H_2O + 5[O]$$

$$\left[\text{Ew of KMnO}_4 \text{ in acidic medium} = \frac{Mw}{5} = \frac{158}{5} = 31.6\right]$$

b. In weakly basic or neutral medium, (ionic equation is written in neutral medium).

$$MnO_4^{\Theta} + 8H^{\oplus} + 3e^{\Theta} \longrightarrow MnO_2 + 2H_2O$$
(n factor = 3)  $(E^{\Theta} = +1.69 \text{ V})$ 

Jonic equation in weakly basic medium:  

$$MnO_4^{\ominus} + 2H_2O + 3e^{\ominus} \longrightarrow MnO_2 + 4OH^{\ominus}$$

$$2KMnO_4 + H_2O \longrightarrow 2KOH + 2MnO_2 + 3[O]$$

[Ewof KMnO<sub>4</sub> in neutral medium or weakly basic medium

$$= \frac{Mw}{3} = \frac{158}{3} = 52.6$$

c. In strongly basic medium:

#### Ionic equation:

$$MnO_4^{\Theta} + e^{\Theta} \longrightarrow MnO_4^{2-}$$

$$(n' \text{ factor} = 1) (E^{\Theta} = +0.56 \text{ V})$$

$$2KMnO_4 + 2KOH \longrightarrow 2K_2MnO_4 + H_2O + [O]$$

[Ew of KMnO<sub>4</sub> in strongly basic medium

$$= \frac{Mw}{1} = \frac{158}{1} = 158$$

Note: It is clear that  $[H^{\oplus}]$  influences the reaction. But redox potential and kinetics of the reaction also are important factor.  $MnO_4^{\odot}$  at  $[H^{\oplus}] = 1$  should oxidise water  $(E^{\Theta})$  oxid for  $H_2O = -1.23$  V) but in practice the reaction is extremely slow unless either Mn<sup>2+</sup> ions are present or the temperature is raised.

**d.** A few important oxidising reaction of  $KMnO_4$  are given below in acid solutions.

The full ionic reaction is obtained by adding the halfreaction for  $MnO_4^{\ \odot}$  in different medium (acidic, basic and neutral) to the half-reaction of the reducing agent, balancing wherever necessary.

- i. It oxides  $I^{\ominus}$  to  $I_2$ .  $2MnO_4^{\ominus} + 10I^{\ominus} + 16H^{\oplus} \longrightarrow 2Mn^{2+} + 8H_2O + 5I_2$
- ii. It oxides  $Fe^{2+}$  ion (green) to  $Fe^{3+}$  ion (yellow)  $5Fe^{2+} + 5MnO_4^{\ominus} + 8H^{\oplus} \longrightarrow Mn^{2+} + 4H_2O + 5Fe^{3+}$
- iii. It oxides oxalate ion  $(C_2O_4^{\ 2-})$  or oxalic acid

$$(H_2C_2O_4)$$
 at  $CO_2$  at 333 K.

$$(C_2O_4^{\ 2})$$
 at  $CO_2$  at 333 K.  
 $(C_2O_4^{\ 2} \longrightarrow 2CO_2 + 2e^{\Theta})$   
 $5C_2O_4^{\ 2} + 2MnO_4^{\ \Theta} + 16H^{\oplus} \longrightarrow 2Mn^{2+} + 8H_2O$   
 $+ 10CO_2$ 

End point of reaction is from colourless to light pink.

iv. It oxides sulphides ion (S $^{2-}$ ) or  $H_2S$  to S

$$(S^{2-} \longrightarrow S + 2e^{\Theta})$$

$$5S^{2-} + 2MnO_4^{\Theta} + 16H^{\Theta} \longrightarrow 2Mn^{2+} + 8H_2O + 5S$$

v. It oxides sulphite ion (SO<sub>3</sub><sup>2-</sup>) or sulphurous acid  $H_2SO_3$ ) to sulphate ( $SO_4^{2-}$ ) or  $H_2SO_4$ .

$$(SO_3^{2-} + H_2O \longrightarrow SO_4^{2-} + 4H^{\oplus} + 2e^{\Theta})$$

$$5SO_3^{2-} + 2MnO_4^{\Theta} + 6H^{\oplus} \longrightarrow 2Mn^{2+} + 3H_2O + 5SO_4^{2-}$$

vi. It oxides nitrite  $(NO_2^{\ominus})$  to nitrate  $(NO_3^{\ominus})$ 

$$(NO_2^{\ominus} + H_2O \longrightarrow NO_3^{\ominus} + 2H^{\oplus} + 2e^{\ominus})$$

$$5NO_2^{\ominus} + 2MnO_4^{\ominus} + 6H^{\oplus} \longrightarrow 2Mn^{2+} + 3H_2O + 5NO_3^{\ominus}$$

vii. It oxides arsenite  $(AsO_3^{3-})$  to arsenate  $(AsO_4^{3-})$ 

$$(AsO_3^{2-} + H_2O \longrightarrow AsO_4^{3-} + 2H^{\oplus} + 2e^{\Theta})$$

$$5AsO_3^{3-} + 2MnO_4^{\Theta} + 6H^{\oplus} \longrightarrow 2Mn^{2+} + 3H_2O + 5AsO_4^{3-}$$

viii. It oxides hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) to O<sub>2</sub>

$$(H_2O_2 \longrightarrow O_2 + 2H^{\oplus} + 2e^{\Theta})$$

$$2\text{MnO}_4^{\ominus} + 5\text{H}_2\text{O}_2 + 6\text{H}^{\oplus} \longrightarrow 5\text{O}_2 + 2\text{Mn}^{2+} + 8\text{H}_2\text{O}$$

ix. It oxides halogen acid (HX) or  $X^{\Theta}$  ion to  $X_2$ 

(where X = Cl, Br, I), e.g., 
$$Cl^{\Theta}$$
 is oxidised to  $Cl_2$ 

$$(2Cl^{\Theta} \longrightarrow Cl_2 + 2e^{\Theta})$$

$$2MnO_4^{\Theta} + 10Cl^{\Theta} + 16H^{\oplus} \longrightarrow 2Mn^{2+} + 5Cl_2 + 8H_2O$$

**x.** It oxides  $SO_2$  to  $SO_4^{2-}$ 

$$(SO_2 + 2H_2O \longrightarrow SO_4^{2-} + 4H^{\oplus} + 2e^{\Theta})$$

$$2MnO_4^{\ominus} + 5SO_2 + 2H_2O \longrightarrow 2Mn^{2+} + 5SO_4^{2-} + 4H^{\ominus}$$

xi. It oxides 
$$\operatorname{Sn}^{2+}$$
 to  $\operatorname{Sn}^{4+}$   $(\operatorname{Sn}^{2+} \longrightarrow \operatorname{Sn}^{4+} + 2e^{\Theta})$ 

$$2MnO_4^{\ominus} + 5Sn^{2+} + 16H^{\oplus} \longrightarrow 2Mn^{2+} + 5Sn^{4+} + 8H_2O$$

xii. It oxides ethyl alcohol (CH3CH2OH) to acetaldehyde (CH<sub>3</sub>CHO)

$$(C_2H_5OH \longrightarrow CH_3CHO + 2H^{\oplus} + 2e^{\Theta})$$

$$2MnO_4^{\Theta} + 5C_2H_5OH + 6H^{\oplus} \longrightarrow 2Mn^{2+} + 5CH_3CHO + 8H_2O$$

xiii. It oxides acetaldehyde (CH3CHO) to acetic acid (CH<sub>3</sub>COOH)

$$(CH_3CHO + H_2O \longrightarrow CH_3COOH + 2H^{\oplus} + 2e^{\Theta})$$
  
 $2MnO_4^{\Theta} + 5CH_3CHO + 6H^{\oplus} \longrightarrow 2Mn^{2+} +$   
 $5CH_3COOH + 3H_2O$ 

e. In neutral or faintly alkaline solutions: KMnO<sub>4</sub> acts as a moderate oxidising agent in neutral aqueous solution because of the reaction.

$$2KMnO_4 + H_2O \longrightarrow 2KOH + 2MnO_2 + 3[O]$$

or 
$$MnO_4^{\ominus} + 2H_2O + 3e^{\ominus} \longrightarrow MnO_2 + 4O\overset{\ominus}{H}$$

During the course of reaction, the alkali (OH ions) generated makes the medium alkaline even when the reaction is started in neutral medium.

Some oxidising properties of KMnO<sub>4</sub> in the neutral or faintly alkaline medium are given below:

i. It oxides iodide  $(I^{\Theta})$  to iodate  $(IO_3^{\Theta})$ 

$$I^{\ominus} + 6O\overset{\ominus}{H} \longrightarrow IO_3^{\ominus} + 3H_2O + 6e^{\ominus}$$

$$MnO_4^{\ominus} + 2H_2O + 3e^{\ominus} \longrightarrow MnO_2 + 4O\overset{\ominus}{H}] \times 2$$

$$2MnO_4^{\ominus} + H_2O + I^{\ominus} \longrightarrow 2MnO_2 + 2O\overset{\ominus}{H} + IO_3^{\ominus}$$

ii. It oxidises thiosulphate 
$$(S_2O_3^{\ 2^-})$$
 to  $SO_4^{\ 2^-}$ 

$$S_2O_3^{\ 2^-} + 10OH \longrightarrow 2SO_4^{\ 2^-} + 5H_2O + 8e^{\Theta}] \times 3$$

$$\underbrace{MnO_4^{\ \Theta} + 2H_2O + 3e^{\Theta} \longrightarrow MnO_2 + 4OH}_{\otimes} \times 8$$

$$8MnO_4^{\ \Theta} + 3S_2O_3^{\ 2^-} + H_2O \longrightarrow 8MnO_2 + 6SO_4^{\ 2^-}$$

$$+ 2OH$$

iii. It oxidises manganous (Mn<sup>2+</sup>) salt to MnO<sub>2</sub> in neutral medium. The presence of ZnSO<sub>4</sub> or ZnO catalyses the oxidation.

**Note:** The ionic equation for the reduction of MnO<sub>4</sub> in neutral medium is used

$$\frac{\text{MnO}_4^{\ominus} + 4\text{H}^{\oplus} + 3e^{\ominus} \longrightarrow \text{MnO}_2 + 2\text{H}_2\text{O}] \times 2}{\text{Mn}^{2^+} + 2\text{H}_2\text{O} \longrightarrow \text{Mn}^{2^+} + 2\text{H}_2\text{O} \longrightarrow \text{Mn}^{2^+} + 2\text{H}_2\text{O} \longrightarrow 5\text{MnO}_2 + 4\text{H}^{\oplus}} \times 3}$$

$$\frac{\text{MnO}_4^{\ominus} + 3\text{Mn}^{2^+} + 2\text{H}_2\text{O} \longrightarrow 5\text{MnO}_2 + 4\text{H}^{\oplus}}{\text{MnO}_4^{\ominus} + 3\text{Mn}^{2^+} + 2\text{H}_2\text{O} \longrightarrow 5\text{MnO}_2 + 4\text{H}^{\oplus}}$$

iv. It oxidises olefinic compounds to basic medium to glycols. The pink colour of KMnO<sub>4</sub> is discharged, and blackish brown precipitate of MnO<sub>2</sub> is obtained. This test is known as Baeyer's test for unsaturation and cold alkaline KMnO<sub>4</sub> is called Baeyer's reagent.

#### Note:

Titration of KMnO<sub>4</sub> in presence of HCl is unsatisfactory, since HCl is oxidised to Cl<sub>2</sub>.
 (2Cl<sup>Θ</sup> → Cl<sub>2</sub> + 2e<sup>Θ</sup>)

Moreover, the nascent oxygen produced from  $KMnO_4 + HCl$  is partly used up to oxidise HCl to  $Cl_2$ .

 HNO<sub>3</sub> itself is an oxidising agent which reacts with reducing agents and therefore cannot be used in KMnO<sub>4</sub> in acidic medium. 3. H<sub>2</sub>SO<sub>4</sub> is suitable for the titration of KMnO<sub>4</sub> in acidic medium, since it does not react with KMnO<sub>4</sub> or the reducing agent used. This is because SO<sub>4</sub><sup>2-</sup> ion cannot be oxidised further since sulphur in SO<sub>4</sub><sup>2-</sup> ion is present in its maximum oxidation state of +6. Moreover, H<sub>2</sub>SO<sub>4</sub> does not give any nascent oxygen of its own to oxidise the reducing agent.

## 6.23.1 STRUCTURES OF MnO<sub>4</sub> AND MnO<sub>4</sub> 2-

- 1. Both  $MnO_4^{\Theta}$  and  $MnO_4^{2-}$  are  $sp^3$  hybridised and  $h_{enc}$  four O-atoms are arranged tetrahedrally around Mn atom as shown in Figure 6.10.
- 2. Purple MnO<sub>4</sub> is diamagnetic and green MnO<sub>4</sub> paramagnetic with one unpaired electron.
- 3. MnO<sub>4</sub> is in +7 O.S. with 3d<sup>0</sup> configuration and hence is diamagnetic, MnO<sub>4</sub><sup>2-</sup> is in +6 oxidation state with 3d<sup>1</sup> configuration and hence is paramagnetic.
- 4. The deep purple colour of KMnO<sub>4</sub> is not due to *d*–*d* transition but due to charge transfer (from O to Mn) reducing the oxidation state of Mn from +7 to +6 momentarily. (LMCT) Ligand to metal charge transfer)
- **5.** Both  $MnO_4^{\ominus}$  and  $MnO_4^{2-}$  have  $(p\pi d\pi)$  multiple bonding. The bonding takes place by overlap of *p*-orbitals of 0-atom with *d*-orbitals of Mn-atom.

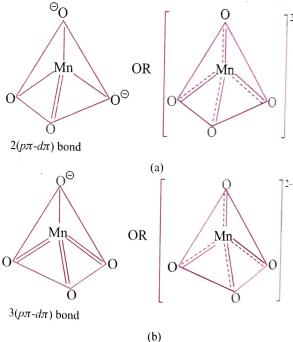


Fig. 6.10 (a) Tetrahedral structure of green MnO<sub>4</sub> <sup>2-</sup> ion and (b) Tetrahedral structure of purple MnO<sub>4</sub> oion

Uses:

1. It is often used in volumetric analysis for the estimation of

- It is often used in volumetric analysis for the estimation of ferrous salts, oxalates, iodides and hydrogen peroxide.

  Note: It is not a primary standard because it is difficult to obtain it in the pure state and free from traces of MnO<sub>2</sub>. It is, therefore, always first standardised with a standard solution of oxalic acid.
- 2. It is used as a strong oxidising agent in the laboratory as well as in industry. It is a favourite and effective oxidising agent used in organic synthesis. Alkaline potassium permanganal is used for testing unsaturation in organic chemistry and is known as Baeyer's reagent.

Because of its strong oxidising power, it is also used for bleaching of wool, cotton, silk and other textile fibres and gls0 for decolourisation of oils.

potassium permanganate is also widely used as a disinfectant and germicide. A very dilute solution of permanganate is and germanganate is specifically and for washing wounds and gargling for mouth sore. It is also used for purifying water of stinking wells.

5 Use of KMnO<sub>4</sub> in redox-titrations: KMnO<sub>4</sub> is a powerful and versatile oxdising agent and is widely used for titration against reducing agents like oxalic acid Mohr's salt. During the titration, the reduction of KMnO<sub>4</sub> by a reducing agent e.g., oxalic acid or Mohr's salt, produces manganous ions which are nearly colourless.

$$\text{MnO}_4^{\Theta} + 8\text{H}^{\oplus} + 5e^{\Theta} \longrightarrow \text{Mn}^{2+} + 4\text{H}_2\text{O}$$

As the titration proceeds and when the whole of the reducing agent is consumed up, then the addition of an excess drop of KMnO<sub>4</sub> solution gives its own colour (pink) to the solution. Therefore, at the end point the colour changes from colourless to pink. Thus, KMnO<sub>4</sub> acts as a self-indicator.

### 6,24 THE INNER TRANSITION **ELEMENTS (f-BLOCK) (OR) RARE EARTH ELEMENTS**

#### 6.24.1 GENERAL CHARACTERISTICS

The elements in which the last electron (also called differentiating electron) enter the antepenultimate energy level, i.e. (n-2)Autitals are called f-block elements. These elements have also icalled inner transition elements. This is because the last electron in them enters into (n-2) f-orbitals, i.e., inner to the raultimate energy level and they form a transition series within transition series (d-block elements). Their general electronic configuration is:

$$(n-2) f^{1-14} (n-1) d^{0-1} ns^2$$

Thus, they have three incomplete shells, viz., (n-2), (n-1) and

#### **6.24.2 CLASSIFICATION OF** *f***-BLOCK ELEMENTS**

Depending upon whether the last electron enters a 4f-orbital or a 5f-orbital, the f-block elements have been divided into two series as follows:

- 1. Lanthanoids: The elements in which the last electron enters one of the 4f-orbitals are called 4f-block elements or first inner transition series. These are also called lanthanides or lanthanons or lanthanoids because they come immediately after lanthanum. Earlier, these 14 elements were called rare earth.
- 2. Actinoids: The elements in which the last electron enters one of the 5f-orbitals are called 5f-block elements or second inner transition series. These are also called actinides or actinons or actinoids because they come immediately after actinium.

3. Lanthanum, though a d-block element, is included in the

- lanthanoid series because it closely resembles lanthanoids for which the general symbol Ln is often used. Similarly, actinium is also included in the actinoid series. Further the study of lanthanoids is comparatively easier because they show only one stable oxidation state. On the other hand, the chemistry of actinoids is much more complicated partly because they show a wide range of oxidation states and partly because they are radioactive.
- 4. They are also referred as rare earth elements, because their occurrence in earth is very rare. Cerium (Ce) constitutes about  $3 \times 10^{-4}$  % of earth's crust which is most commonly occurring lanthanoid.
- 5. The most common mineral containing lanthanoids is 'monazite sand'. It is mainly lanthanoid orthophosphate.

ble 6.13 Electronic configuration and radii of lanthanum and lanthanoids (Ln)

mic	Name	Cumbal		Electronic confi	guration*		Oxidation Radii/p		i/pm
nber	Name	Symbol	Ln	Ln <sup>2+</sup>	Ln <sup>3+</sup>	Ln <sup>4+</sup>	states	Ln	Ln <sup>3+</sup>
7	Lanthanum	La	$5d^16s^2$	$5d^1$	$4f^0$		+3	187	106
8		700	$4f^15d^16s^2$	$4f^2$	$4f^{1}$	4f 0	+3, +4	183	103
9	Cerium	Ce		$4f^3$	$4f^2$	$4f^{1}$	+3, +4	182	101
_	Praseodymium	Pr	$4f^36s^2$	4f <sup>4</sup>	$4f^3$	$4f^2$	+2, +3, +4	181	99
0	Neodymium	Nd	$4f^46s^2$	J		7)	+3	181	98
1	Promethium**	Pm	$4f^56s^2$	4f <sup>5</sup>	4f <sup>4</sup>				96
2	Samarium	Sm	$4f^66s^2$	4f <sup>6</sup>	4f <sup>5</sup>		+2, +3	180	
3	Europium	Eu	$4f^76s^2$	4f <sup>7</sup>	4f <sup>6</sup>		+2, +3	199	95
4	Gadolinium	Gd	$4f^{7}5d^{1}6s^{2}$	$4f^7 5d^1$	4f <sup>7</sup>		+3	180	94
5	Terbium	Tb	$4f^96s^2$	4f <sup>9</sup>	4f 8	$4f^7$	+3, +4	178	92
6	Dysprosium		$4f^{10}6s^2$	4f 10	4f 9	4f <sup>8</sup>	+3, +4	177	91
7		Dy	$4f^{11}6s^2$	41 11	4f 10		+3	176	89
8	Holmium	Но		4f 12	4f 11		+3	175	88
9	Erbium	Er	$4f^{12}6s^2$	$4f^{-13}$	$4f^{12}$		+2, +3	174	87
0	Thulium	Tm	$4f^{13}6s^2$				-		86
-	Ytterbium	Yb	$4f^{14}6s^2$	4f 14	4f 13		+2, +3	173	80
1	Lutetium	Lu	$4f^{14}5d^{1}6s^{2}$	$4f^{14}5d^{1}$	4f 14	,	+3		_

The properties of the properti \*\*Promethium is the only synthetic (man made) radioactive lanthanoid  $v_{\text{ote: Elements}}^{\text{avg electrons}}$  outside [Xe] core are mulcated. Elements with  $4f^2$  and  $4f^8$  electronic configuration are not known.

#### Note:

- 1. From the electronic configuration of Ln given in Table, it is clear that electron can shift between f- and d-orbitals depending upon the stability of electronic configuration.
- 2. As we move higher in energy levels, energy gap is decreasing and shifting of electron is very much possible.

#### 6.24.3 ATOMIC AND IONIC SIZES

There is gradual steady decrease in atomic/ionic radii along the lanthanoid series from La to Lu and La<sup>3+</sup> to Lu<sup>3+</sup>. This regular decrease in the sizes of the atoms and ion with increasing atomic number is called **lanthanoid contraction** (Figure 6.11).

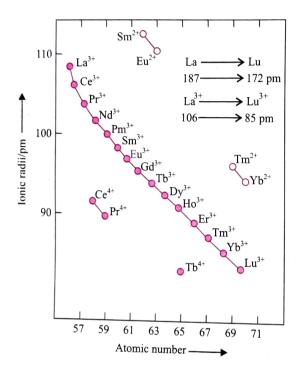


Fig. 6.11 Trends in ionic radii of lanthanoids

**Explanation:** The overall decrease in atomic and ionic radii from lanthanum to lutetium (the lanthanoid contraction). It has far reaching consequences in the chemistry of the third transition series of the elements. The decrease in atomic radii is not quite regular as it is regular in  $M^{3+}$  ions. This contraction is, of course, similar to that observed in an ordinary transition series and is attributed to the same causing the imperfect shielding of one electron by another in the same sub-shell. However, the shielding of one 4f electron by another is less than one d electron by another. Hence with the increase in nuclear charge along the series, there is fairly regular decrease in the sizes with increasing atomic number.

The cumulative effect of the contraction of lanthanoid series, known as lanthanoid contraction, causes the radii of the members of the third transition series to be very similar to those of the corresponding members of the second series. The almost identical radii of Zr (160 pm) and Hf (159 pm) a consequence of the lanthanoid contraction, account for their occurrence together in nature and for the difficulty faced in their separation.

## 6.24.4 CONSEQUENCES OF LANTHANOIDS CONTRACTION

- 1. Difficulty in separation of lanthanoids: Since the change in ionic radii (size of the ions) in lanthanides is very small, their chemical properties are similar. This makes the separation of the elements in the pure state difficult. However, lanthanide contraction results in slight difference in the size of lanthanides which results in the differences in properties like solubility, complex ion formation, hydration etc. These differences enable the separation of individual lanthanide elements by (i) valency change and (ii) ion exchange chromatographic methods by using zeolites
  - i. Valency change: A few lanthanides have oxidation states of +4 or +2. The properties of Ln<sup>4+</sup> or Ln<sup>2+</sup> are so different from those of Ln<sup>3+</sup> that separation is fairly easy.

Ce can be separated from lanthanide mixtures quite easily as it is the only lanthanide which has  ${\rm Ln}^{4+}_{\rm ions}$  stable in aqueous solution.

Oxidising a solution containing a mixture of Ln<sup>3+</sup> ions with NaOCl under alkaline conditions produces Ce<sup>4+</sup>. Because of the higher charge, Ce<sup>4+</sup> is much smaller and less basic than Ce<sup>3+</sup> or any other Ln<sup>3+</sup>. The Ce<sup>4+</sup> is separated by carefully controlled precipitation of CeO, or Ce(IO<sub>3</sub>)<sub>4</sub>, leaving the trivalent ions in solution.

Alternatively Ce<sup>4+</sup> can readily be extracted from other Ln<sup>3+</sup> lanthanides by solvent extraction in HNO<sub>3</sub> solution using tributyl phosphate. Ninety-nine per cent pure Ce can be obtained in one stage from a mixture containing 40% Ce.

Valency change is still useful method for purifying Ce and Eu despite the advent in recent years of ion exchange.

- ii. Ion exchange chromatographic methods by using zeolites: Ion exchange method is based on the fact that hydrated radii of lanthanoid ions increase with increasing atomic number. Thus, when a solution containing several lanthanoid ions passes slowly through the column of cation exchange resin, the heavier members will come through first.
- 2. Similarity in size of elements belonging to same group of second and third transition series: In general, the size of the atoms increases down a group (↓). However, whereas the size of the atom of any element lying in the second transition series is larger than that of the atom of the element lying in the same group of the transition series (as expected), the size of any atom of the third transition series (after lanthanum) is nearly same as that of the atom of the element lying in the same group of the second transition series. A few elements of the 1st, 2nd and 3rd transition series along with their covalent radii are given in Table 6.14.

The similarity in size of the atoms of the elements belonging to the same group of the 2nd and 3rd transition series (after lanthanum) (e.g.  $r_{\rm Zr} \approx r_{\rm Hf}$  and  $r_{\rm Nb} \approx {\rm Ta}$ ) is evidently due to the effect o lanthanide contraction.

#### 6.14 Covalent radii of some transition elements

the -				
Group No.	3	4	5	6
3d series	Sc (21) 144 pm	Ti (22) 132 pm	V (23)	Cr (24)
<sub>4d</sub> series	Y(39)	Zr (40)	122 pm Nb (41)	117 pm Mo (42)
	162 pm La (57)	145 pm Hf (72)	134 pm Ta (73)	129 pm
dseries	169 pm	144 pm	134 pm	W (74) 130 pm
		— 14 Lan	thanide elem	ents (58–71

1 Effect on the basic strength of hydroxides: As the size of the lanthanide ions decreases from La<sup>3+</sup> to Lu<sup>3+</sup>, the covalent character of the hydroxides increases and hence the basic strength decreases (Fazan's rule). Thus La(OH)<sub>3</sub> is most basic whereas Lu(OH)<sub>3</sub> is least basic.

#### 6.24.5 OXIDATION STATE

- 1. The most predominant and stable oxidation state (O.S.) of lanthanoids is +3.
- 2. However, +2 and +4 ions in solution and solid compounds also exist.
- 3. Like irregularity in I.E., the irregularity in O.S. arises mainly from the stable electronic configuration of half-filled or fully filled 4f-orbitals, for example

 $\mathrm{Eu}^{2+}(4f^7)$ ,  $\mathrm{Yb}^{2+}(4f^{14})$ ,  $\mathrm{Ce}^{4+}(4f^0)$  and  $\mathrm{Tb}^{4+}(4f^7)$ 

Note: Lanthanoids show limited number of O.S. because there is a large energy gap between 4f and 5d subshells.

- 4. Both +2 and +4 O.S. have a tendency to revert back to more stable O.S. of +3.
- 5.  $E_{\text{Ce}^{4+}/\text{Ce}^{3+}}^{\Theta} = +1.74 \text{ V}$ , which suggests that is can oxidise water, still it is used as an oxidising agent in analytical chemistry because the oxidation of H<sub>2</sub>O by Ce<sup>4+</sup> is kinetically a very slow process.
- 6. Pr, Nd, Tb and Dy also exhibit +4 O.S. but only in oxides,
- 7. Eu<sup>2+</sup> and Yb<sup>2+</sup> have a tendency to undergo oxidation to +3 0.S. and hence acts as reducing agent in aqueous solutions.
- 8. Likewise Ce<sup>4+</sup> and Tb<sup>4+</sup> have a tendency to undergo reduction to +3 O.S. and hence acts as oxidising agent.
- 9. Like Eu, Sm exhibits both +2 and +3 O.S.
- 10. Exceptions: As shown in Table 6.13, some elements show an O.S. of +2 and +4, even though their ions do not have  $f^0$ ,  $f^7$  or  $f^{14}$  configuration, e.g.,  $Pr^{4+}(4f^1)$ ,  $Nd^{2+}(4f^4)$ ,  $Nd^{4+}(4f^2)$ ,  $Sm^{2+}(4f^6)$ ,  $Dy^{4+}(4f^8)$  etc.

## 6.24.6 PHYSICAL PROPERTIES

- 1. All the lanthanoids are silvery white soft metals and tarnish rapidly in the air. Their hardness increases with increasing atomic number. Sarmarium (Sm) is exceptionally hard like steel.
- 2. All of them have typical metallic structure and are good conductors of heat and electricity.
- 3. They have high densities which lie in the range from 6.77 to 9.74 g cm<sup>3</sup>. Density and other properties vary smoothly

- with increasing atomic number except for Eu and Yb and occasionally for Sm and Tm.
- 4. They have high melting points in the range from 1000 to 1200 K except samarium which has a very high melting point of 1623 K.
- 5.  $La^{3+}(f^0)$ ,  $Ce^{4+}(4f^0)$  and  $Lu^{3+}(4f^{14})$  configuration have no unpaired electrons and are diamagnetic. All other 4f elements / ions contain unpaired electrons and are therefore paramagnetic.
- 6. Lanthanoids differ from transition elements in the fact that their magnetic moments do not obey 'spin only' formula, viz.,  $\mu_{\text{eff}} = \sqrt{n(n+2)}$  BM, where *n* is the number of unpaired electrons. This is because in case of transition elements, the orbital contribution is quenched by the electric field of the environment but in case of lanthanoids, 4f orbitals are much more penetrated towards nucleous than 'd' orbitals therefore orbital contribution is not ignored. Hence, their magnetic moment is calculated by considering spin as well as orbital contribution, i.e.,

$$\mu_{(S+L)} = \sqrt{4S(S+1) + L(L+1)}$$
 BM

where S is spin quantum number and L is orbital quantum number.

The magnetic moment calculated by spin only formula works with  $La^{3+}(f^0)$ ,  $Gd^{3+}(f^7)$  and  $Lu^{3+}(f^{14})$ .  $La^{3+}$  and  $Lu^{3+}$  have no unpaired electrons (n = 0) therefore  $\mu_{n} = 0$ . Gd<sup>3+</sup> have 7 unpaired electrons (n = 7) and

$$\mu_{\rm s} = \sqrt{7(7+2)} = \sqrt{63} = 7.9 \text{ BM}$$

The other lanthanide ions do not obey the simple relationship. The 4f electrons are well shielded from external fields by the overlying 5s and 5p electrons. Thus the magnetic effect of the motion of the electron in its orbital is not quenched out. Thus the magnetic moments must be calculated taking into account both the magnetic moment from the unpaired electron spins and that from the orbital motion. This also happens with the second and third row transition elements. However, the magnetic properties of the lanthanides are fundamentally different from those of the transition elements. In the lanthanides the spin contribution S and orbital contribution L couple together to give a new quantum number J.

J = L - S when the shell is less than half full and J = L = S when the shell is more than half full The magnetic moment  $\mu$  is calculated in Bohr magnetons (BM) by

$$\mu = g\sqrt{J(J+1)}$$
 where  $g = 1\frac{1}{2} + \frac{S(S+1) - L(L+1)}{2J(J+1)}$ 

Figure 6.12 shows the calculated magnetic moments for the lanthanide ions in +3 O.S. momentum formula using both the simple spin only formula and the coupled spin plus orbital momentum formula.

The unusual shape of the spin plus orbital motion curve arises because of Hund's third rule. When the f level is less than half full the spin and orbital momenta contributions work in opposition (J = L - S). When the f shell is more than half full they work together (J = L + S).

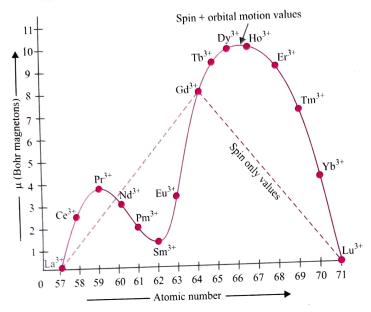


Fig. 6.12 Paramagnetic moments of  ${\rm Ln}^{3+}$  lanthanide ions at 300 K. Spin only values are shown as a broken line, and the spin plus orbital motion as solid lines

The calculated and observed magnetic moment values of La<sup>3+</sup> and Ln<sup>3+</sup> ions are given in Table.

Table 6.15 Magnetic moments of La<sup>3+</sup> and Ln<sup>3+</sup> ions

Symbol and atomic number	Electronic structure of Ln <sup>3+</sup>		ic moment BM)
72.7		Calculated	Observed
La (57)	$4f^0$	0	0
Ce (58)	4f 1	2.54	2.3-2.5
Pr (59)	4f <sup>2</sup>	3.58	3.4–3.6
Nd (60)	$4f^3$	3.62	3.5-3.6
Pm (61)	4f 4	2.68	2.7
Sm (62)	4f <sup>5</sup>	0.84	1.5-1.6
Eu (63)	4f <sup>6</sup>	0	3.4-3.6
Gd (64)	$4f^7$	7.94	7.8-8.0
Tb (65)	4f 8	9.72	9.4-9.6
Dy (66)	4f <sup>9</sup>	10.63	10.4-10.5
Ho (67)	4f 10	10.60	10.3-10.5
Er (68)	4f 11	9.57	9.4-9.6
Tm (69)	4f 12	7.63	7.1-7.4
Yb (70)	4f 13	4.50	4.4-4.9
Lu (71)	4f 14	0	0

7. The lanthanoids are silvery white metals. However, most of the trivalent metal ions are coloured, both in the solid state and in aqueous solution. This is due to the partly filled f-orbitals which permit f-f transition.

 $La^{3+}(4f^0)$ ,  $Ce^{4+}(4f^0)$ ,  $Lu^{3+}(4f^{14})$  and  $Yb^{2+}(4f^{14})$  are colourless because of no f-f transitions is possible, but the rest do so. However, absorption bands are narrow because of the excitation within f-levels.

Lanthanoid ions with n f electrons have a similar colouidade fto those with (14 - n) f electrons, e.g.,  $La^{3+}$  and  $Lu^{3+}$  a

- 8. IE<sub>1</sub> of lanthanoids are around 600 kJ mol<sup>-1</sup> and the  $IE_2 \approx 1200 \text{ kJ mol}^{-1}$  which are comparable with those of Ca. The variation of the IE<sub>3</sub> shows that just as in  $case_{00}$ 3d transition series, the loss of the first two electrons is accompanied by exchange enthalpy. Further, the loss of third electron is easier, i.e., IE<sub>3</sub> is low if it leads to stable empty half-filled or completely filled configuration, as indicated by the abnormally low IE<sub>3</sub> values of La, Gd and Lu.
- 9. Their standard reduction potentials, i.e.,  $E_{\text{M}^{3+}(aq)/M(s)}^{\Theta}$ values for the half reaction lie in the range from  $-2.2 \frac{1}{10}$ -2.4 V, the only exception being europium (Eu) for which the  $E^{\Theta}$  value is -2.0 V.
- 10. They are highly electropositive because of their low ionisation enthalpies.
- 11. They readily lose electrons and are thus good reducing agents.
- 12. They do not have much tendency to form complexes due to low charge density because of their large size. The tendency to form complexes and their stability increases with increasing atomic number.

#### 6.24.7 CHEMICAL PROPERTIES

The first few members of the series are quite reactive, almost like calcium. However, with increasing atomic number, their behaviour becomes similar to that of aluminium.

- 1. They combine with H<sub>2</sub> on gentle heating.
- 2. When heated with carbon, they form carbides, e.g., Ln<sub>3</sub>C.  $Ln_2C_3$  and  $LnC_2$ .
- 3. They burn in halogens to form halides.
- **4.** They react with dilute acids to liberate H<sub>2</sub> gas.
- 5. They form oxides and hydroxides of the type M<sub>2</sub>O<sub>3</sub> and M(OH)<sub>3</sub> which are basic like alkaline earth metal oxides and hydroxides. The hydroxides are definite compounds. not just hydrated oxides.

The general reactions are shown in Figure 6.13.

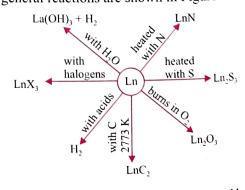


Fig. 6.13 Chemical reactions of the lanthanoids

#### 6.24.8 Uses of Lanthanoids

1. Lanthanoids are used in the production of alloy steels to improve the strength and workability of steel. A well known alloy is mischmetal which has the following composition

Name of the alloys	Composition
Mischmetal	Lanthanoid metals = 95%
1,7	(about 40% La, 50% Ce and the rest other lanthanoids)
	Iron = 5%
	S, C, Ca  and  Al = traces

The maximum amount of mischemetal is used in making a magnesium-based alloy (i.e., Mg mixed with about 3% mischmetal to increase the strength of Mg). It is called pyrophoric alloy.

Name of the alloys	Composition
pyrophoric alloy:	Ce = 45.5%
are used in	La + Nd = 44%
-ling billets, shells	Fe = 4.5%
1 Labter IIIIII	Al = 0.5%
(because it emits spark when struck)	Ca, Si and C = traces

- 2. Because of their paramagnetic and ferromagnetic properties, their compounds are used in making magnetic and electronic devices.
- 3. Their oxides e.g., La<sub>2</sub>O<sub>3</sub> are used as phosphor for television screens and similar fluorescing surfaces.

Mixed oxides of lanthanoids are used as catalysts in petroleum cracking.

## ILLUSTRATION 6.14

Name a member of the lanthanoid series which is well known to exhibit +4 oxidation state.

Sol. Cerium (Z = 58)

## 6.25 ACTINOIDS

1. The actinoids include 14 elements from the (thorium) to Lr (lawrencium). The names, symbols, valence electronic configuration and some properties are given in Table.

rible 6.16 Some properties of actinium and actinoids

Atomic	Name	Symbol		Electronic configuration*				
umber	per of the properties	e Charles we	M	M <sup>3+</sup>	M <sup>4+</sup>	M <sup>4+</sup>	M <sup>3+</sup>	M <sup>4+</sup>
89	Actinium	Ac	$6d^17s^2$	5d <sup>0</sup>	4f 0		111	
90	Thorium	Th	$6d^27s^2$	5f <sup>1</sup>	$4f^{1}$	5f 0		99
91	Protactinium	Pa	$5f^26d^17s^2$	$5f^2$	$4f^2$	5f <sup>1</sup>		96
92	Uranium	U	$5f^36d^17s^2$	$5f^3$	$4f^3$	$5f^2$	103	93
93	Neptunium	Np	$5f^46d^17s^2$	$5f^4$	4f 4	$5f^3$	101	92
94	Plutonium	Pu	$5f^{6}7s^{2}$	5f <sup>5</sup>	4f <sup>5</sup>	5f 4	: 100	90
95	Americium	Am	$5f^77s^2$	5f <sup>6</sup>	4f <sup>6</sup>	5f <sup>5</sup>	99	89
96	Curium	Cm	$5f^{7}6d^{1}7s^{2}$	5f <sup>7</sup>	$4f^7$	5f <sup>6</sup>	99	88
97	Berkelium	Bk	$5f^97s^2$	5f <sup>8</sup>	$4f^8$	$4f^7$	98	87
98	Californium	Cf	$5f^{10}7s^2$	5f <sup>9</sup> .	$4f^9$	4f 8	98	86
99	Einstenium	Es	$5f^{11}7s^2$	$5f^{10}$	$4f^{10}$	5f 9		
100	Fermium	Fm	$5f^{12}7s^2$	5f 11	$4f^{11}$	$5f^{10}$		
101	Mendelevium	Md	$5f^{13}7s^2$	$5f^{.12}$	$4f^{12}$	5f 11	_	-
102	Nobelium	No	$5f^{14}7s^2$	5f 13	$4f^{13}$	5f 12		_
103	Lawrencium	Lr	$5f^{14}6d^{1}7s^{2}$	5f <sup>14</sup>	4f 14	$5f^{13}$	-	-

2. The actinoids are radioactive elements. The earlier members have relatively long half lives, ranging from a day to 3 minutes for Lr (Z = 103). The latter members could be prepared only in nanogram quantities. These facts render their study more difficult.

# 625.1 GENERAL ELECTRONIC CONFIGURATION $5f^{1-14} 6d^{0-1} 7s^2$

- 1. All the actinoids have common 7s<sup>2</sup> configuration and variable occupancy of 5f and 6d subshells.
- The 14 electrons are being added into 5f, except in  $\frac{T_h}{Z} (Z = 90)$  but filling of 5f continues again after Th till 5f orbitals are complete Lr (Z = 103).
- 3. The irregularities in the electronic configurations of actinoids like those in the lanthanoids are related to the stabilities of  $f^0$ ,  $f^7$  and  $f^{14}$  configurations, for example, the configuration of Am and Cm are  $5f^7$   $6d^0$   $7s^2$  and  $5f^7$   $6d^1$   $7s^2$  respectively.
- **4.** Berkelium (Bk, Z = 97) also shows an exceptional configuration of  $5d^9 6d^0 7s^2$  which is neither half-filled nor completely filled.

#### 6.25.2 IONIC SIZES

Like lanthanoids, there is a gradual decrease in the size of atoms or M<sup>3+</sup> ions across the series (Table). This is called **actinoid contraction** (like lanthanoid contraction) attributed to poor

shielding effect of the 5*f*-electrons, which results in the decrease of size of M/M<sup>3+</sup>.

This contraction is greater from element to element in this series resulting from poor shielding by 5*f*-electrons.

Moreover, poor shielding effect of 5f-orbital than 4f-orbitals is also due to less penetration effect of 5f-orbitals than 4f-orbitals.

## **6.25.3 OXIDATION STATES OF ACTINOIDS**

 Unlike lanthanoids, actinoids show a large number of oxidation states.

Table 6.17 Oxidation states (O.S.) of actinium and actinoids

Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr
3	(3)	3	3	3	3	3	3	3	3	3	3	3	3	ુ3
14. 1	4	4	4	4	4	(4)	(4)	4					1,	
		5	5	5	5	5								
			6	6	6	6								
		2 6		7	7									4.5

This is because of very small energy gap between 5f, 6d and 7s subshells. Hence, all their electrons can take part in bond formation.

- 2. The dominant oxidation state of these elements is 3 (similar to lanthanoids). Besides +3 state, actinoids also exhibit an oxidation state of +4. Some actinoids show still higher oxidation states.
- 3. The maximum oxidation state first increases up to the middle of the series and then decreases, e.g., it increases from +4 for Th to +5, +6 and +7 for Pa, U and Np but decreases in the succeeding elements.
- **4.** The actinoids resemble lanthanoids in having more compounds in + 3 state than in the + 4 state.
  - However, the compounds in the +3 and +4 state tend to undergo hydrolysis.
- 5. Both 5f and 4f orbitals have similar shapes and they resemble in thier angular part of the wave functions. But 4f orbitals is much more penetrated (or more buried) then 5f orbital towards nucleus. Hence 5f electrons can participate in bond formation to a far greater extent. That is why actinoids have low IE and more reactive than lanthanoids.

#### 6.25.4 PHYSICAL PROPERTIES

- 1. Like lanthanoids, actinoids are metals with silvery appearance.
- The actinoids like lanthanoids have high melting and boiling points. However, they do not show any regular trend with rise in atomic number.
- **3. Density:** All the actinoids except Th and Am have high densities.
- 4. The actinoids have lower ionisation enthalpies than lanthanoids because 5f is less penetrating than 4f and hence is more effectively shielded from the nuclear charge.

- 5. These metals are silvery white. However, actinoid  $cation_{\S}$  are generally coloured. The colour of the cation  $depend_{\S}$  upon the number of 5f-electrons. The cations containing no 5f-electron or having seven 5f-electrons (i.e., exactly half-filled f-subshell) are colourless. The cations containing 2 to 6 electrons in the 5f-subshell are coloured both in the crystalline state as well as in aqueous solution. The colour arises due to f-f transition e.g.  $Ac^{3+}(5f^0) = colourless$ ,  $U^{3+}(5f^3) = Red$ ,  $Np^{3+}(5f^4) = Blue$ ,  $Pu^{3+}(5f^5) = Violet$ ,  $Am^{3+}(5f^6) = Pink$ ,  $Cm^{3+}(5f^7) = Colourless$ ,  $Th^{3+}(5f^0) = Colourless$ , and so on.
- 6. As they have much V greater irregularities in their metallic radii than lanthanoids, they show great structural variability
- 7. Electropositive character: All the known actinoid metals are highly electropositive. They resemble the elements of lanthanoid series in this respect.
- **8. Magnetic behaviour:** Like lanthanoids, the actinoid elements are strongly paramagnetic.

The variation in magnetic susceptibility of actinoids with the increasing number of unpaired electrons is similar to that of lanthanoids but the values are higher for the actinoids than the lanthanoids.

Reducing agents: All the actinoids are strong reducing agents.

## 6.25.5 CHEMICAL PROPERTIES

- 1. They are highly reactive metals especially in the finely divided state.
- 2. All these metals are attacked by hydrochloric acid but the effect of nitric acid is very small due to the formation of a protective oxide layer on their surface.
- 3. Alkalines have no action on them.
- **4.** They combine with most of the non-metals at moderate temperature.
- 5. They react with boiling water to give a mixture of oxide and hydride.

#### 6.25.6 USES OF ACTINOIDS

The three most important actinoids which find uses as such or in the form of their compounds are Th, U and Pu.

- Th is used in atomic reactors and in the treatment of cancer.
   Its salts are used in making incandescent gas mantles.
- 2. U is used as nuclear fuel. Its salts are used in glass industry (for imparting green colour), textile industry, ceramic industry and in medicines.
- 3. Pu is used as fuel for atomic reactors as well as for making atomic bombs.

# 6.25.7 COMPARISON OF LANTHANOIDS AND ACTINOIDS

- 1. Both show mainly an oxidation state of +3.
- 2. Both are electropositive and very reactive.
- 3. Both exhibit magnetic and spectral properties.

4. Actinoids exhibit actinoid contraction like lanthanoid contraction shown by lanthanoids.

siference: Some differences in their properties are shown as:

nit	Jel Cir	Participation	The same shown as.
/	Lanthanoids		Actinoids
h	Besides +3 oxidation state, they show +2 and +4 oxidation states only in few cases.	i.	Besides +3 oxidation state, they show higher states of +4, +5, +6, +7 also.
	Lanthanoid compounds are	ii.	Actinoid compounds are more basic.
	They have less tendency towards complex formation.	iii.	They have greater tendency towards complex formation.
	Most of their ions are colourless.	iv.	Most of their ions are coloured.
V.	Except promothium, they are non-radioactive	v.	They are radioactive.
vi.	Their magnetic properties can be explained easily.	vi.	Their magnetic properties cannot be explained easily, as they are more complex.

# 6.26 SOME APPLICATIONS OF d- AND f-BLOCK ELEMENTS

- 1. Iron and steel (important construction materials) are produced by the reduction of iron oxides. Cr, Mn and Ni are used as alloying metals.
- 2. TiO is used in white pigment.
- 3. MnO<sub>2</sub> is used in dry battery cells.
- 4. Zn and Ni/Cd are also used in battery industry.
- 5. Coinage metals (group 11 elements), Cu, Ag, Au are used as collection items.
  - UK copper coins are copper-coated steel. 'silver' UK coins are Cu/Ni alloy.
- 6.  $V_2O_5$  is used as catalyst in the manufacture of  $H_2SO_4$  by contact process.
- 7. Fe is used as catalyst in the Haber process for the production of NH<sub>3</sub> from N<sub>2</sub>/H<sub>2</sub> mixtures.
- 8. Ni is used as catalyst for the hydrogenation of oils.
- 9. In the Wacker process the oxidation of ethyne to ethanal is catalysed by PdCl<sub>2</sub>.
- 10. Nickel complexes are useful in the polymerisation of alkynes and other organic compounds such as benzene.
- 11. The photographic industry relies on the special light sensitive properties of AgBr.
- 12. Triethyl aluminium [(C<sub>2</sub>H<sub>5</sub>)<sub>3</sub>Al] and TiCl<sub>4</sub> form the basis of Zeigler–Natta type heterogeneous catalyst is used as a catalyst for the low temperature polymerisation of alkenes (i.e. for the synthesis of high density polythene (HDPE) from ethene
- 13. Homogeneous Wilkinson's catalyst [RhCl(Ph<sub>3</sub>P)<sub>3</sub>] is used as a catalyst in the hydrogenation of alkenes.
- 14. Lindlar's catalyst (LC) (Pd + BaSO<sub>4</sub> + S or quinoline in boiling xylene). It is also called poisoned palladium. It is used in the hydrogenation of alkyne to *cis* alkene e.g.,

$$H_3C-C \equiv C-CH_3 \xrightarrow{H_2+L.C.} H_3C \xrightarrow{C} CH_3$$
But-2-yne
$$H_3C-C \equiv C-CH_3 \xrightarrow{Cis-but-2-ene} H_3C$$

It is also used to convert acid halides (RCOX) to aldehydes and the reaction is known as Rosenmund reduction, e.g.

$$CH_3$$
— $C$ — $Cl$ — $H_2$ + L.C.  $CH_3$ CHO

- **15.** P-2 or brown catalyst. It is nickel boride (Ni<sub>2</sub>B). It is also used in the hydrogenation of alkyne to *cis* alkene.
- **16.** Adam's catalyst (Pt/PtO): It is also used for the hydrogenation of alkene to alkane.

$$H_3C-CH=CH_2 \xrightarrow{H_2+Pt/PtO} H_3C-CH_2-CH_3$$

- 17. Finely divided Pt is a black powder and is called platinum black. Finely divided Ag is also black in colour.
- 18. Ist triad of group VIII (8, 9, 10 group) Fe, Co and Ni collectively are called coinage metals. They are ferromagnetic.
- 19. 2nd and 3rd triads of group VIII (8, 9, 10 group), Ru, Rh and Pd (2nd triad), Os, Ir and Pt (3rd triad), collectively are called platinum metals.

## ILLUSTRATION 6.15

- a. A strip of Cu dissolves in FeCl<sub>3</sub>, however Cu cannot displace Fe.
- **b.**  $[CuCl_4]^{2-}$  exists but  $[CuI_4]^{2-}$  does not. Why?

#### Sol.

- a. This is because  $E^{\Theta}_{Fe^{3+}/Fe^{2+}} > E^{\Theta}_{Cu^{2+}/Cu}$   $Cu_{(s)} + 2FeCl_{3(aq)} \longrightarrow 2FeCl_{2(aq)} + 2CuCl_{2(aq)}$ This method is used for making printed circuit boards (PCB's) used in electronic industry.
- **b.**  $I^{\Theta}$  ion is a stronger reducing agent than  $Cl^{\Theta}$  ion, therefore  $I^{\Theta}$  ion reduces  $Cu^{2+}$  to  $Cu^{\Theta}$  ion. As a result  $CuI_2$  is converted into CuI and hence  $[CuI_4]^{2-}$  does not exist.

$$2CuI_2 \longrightarrow 2CuI + I_2$$

## ILLUSTRATION 6.16

- **a.** Why Mn<sup>2+</sup> compounds are more stable than Fe<sup>2+</sup> towards oxidation to their +3 state?
- **b.** Calculate the magnetic moment of  $V^{3+}$  ion.
- c.  $[Ti(H_2O)_6]^{3+}$  gives violet coloured aqueous solution but  $[Mg(H_2O)_6]^{2+}$  solution is colourless.
- **d.**  $[Ti(H_2O)_6]^{3+}$  is coloured whereas  $[Sc(H_2O)_6]^{3+}$  is colourless. Why?

#### Sol.

a. Electronic configuration of  $\text{Mn}^{2+}$  is  $3d^5$  which is half-filled and hence stable. Therefore IF<sub>3</sub> is very high i.e. 3rd electron cannot be lost easily. In case of Fe<sup>2+</sup>, electronic configuration is  $3d^6$ . Hence it can lose one electron easily to give the stable configuration  $3d^5$ .

- **b.**  $V(Z = 23) \Rightarrow 3d^34s^2$ ,  $V^{3+} = 3d^2$  (n = 2) $\mu = \sqrt{n(n+2)} \text{ BM} = \sqrt{2(2+2)} = \sqrt{8} = 2.73 \text{ BM}$
- **c.** In  $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$ , the  $d^1$  electron occupies  $t_{2g}$  orbital in octahedral field. On irradiation with light, the  $t_{2g}$  electron is promoted to  $e_g$  orbital and the resulting absorption band gives violet colour.

In case of  $[Mg(H_2O)_6]^{2+}$  the electronic configuration of  $Mg^{2+}$  is  $1s^2$ ,  $2s^2$ ,  $2p^6$  which does not permit any electronic transition  $(2p \longrightarrow 3s)$  as the energy gap is very large or there does not occur d-d transition of electron. Hence, it gives colourless solution.

**d.** A In  $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$ , the titanium ion is present in  $\text{Ti}^{3+}$  form with  $3d^1$ ,  $4s^0$  configuration. The single unpaired electron of  $3d^1$  orbital makes the compound to show colour. In  $[\text{Sc}(\text{H}_2\text{O})_6]^{3+}$ , scandium is present as  $\text{Sc}^{3+}$ state with  $3d^04s^0$  configuration. Since no electron is present in the 3d and 4s orbitals, it remains colourless.

## ILLUSTRATION 6.17

- **a.** Why Sm<sup>2+</sup>, Eu<sup>2+</sup> and Yb<sup>2+</sup> ions in solutions are good reducing agents but an aqueous solution of Ce<sup>4+</sup> is a good oxidising agent?
- **b.** Why does Mn(II) show maximum paramagnetic character amongst the bivalent ions of the first transition series?
- c.  $La(OH)_3$  is more basic than  $Lu(OH)_3$ . Explain. (Atomic no. of La = 57, Lu = 71)
- **d.** Give reason. Why in moist air copper corrodes to produce a green layer on the surface.
- e. Which of the following ions are expected to be coloured and why? Fe<sup>2+</sup>, Mn<sup>2+</sup>, Cr<sup>3+</sup>.
- f. Why Zn<sup>2+</sup> salts are white while Ni<sup>2+</sup> salts are blue?

### Sol.

- a. The most stable oxidation state of lanthanides is +3 hence ions in +2 state tend to change to +3 state by loss of electron and those in +4 state tend to change to +3 state by gain of electron.
- **b.** Mn<sup>2+</sup> has maximum number of unpaired electrons.
- c. As the size of lanthanide ions decreases from La<sup>3+</sup> to Lu<sup>3+</sup>, the covalent character of the hydroxides increases. Hence the basic strength decreases from La(OH)<sub>3</sub> to Lu(OH)<sub>3</sub>.
- **d.** Copper in presence of moisture oxygen and carbon dioxide of atmosphere is converted into basic carbonate which is deposited as green layer on surface.

$$2Cu + CO_2 + H_2O + O_2 \longrightarrow Cu(OH)_2CuCO_3$$

- e.  $Fe^{2+}$ ,  $Mn^{2+}$ ,  $Cr^{3+}$  are coloured due to d-d transition of electron takes place.
- **f.**  $Zn^{2+}$  has completely filled *d*-orbitals  $(3d^{10})$  while Ni<sup>2+</sup> has incompletely filled *d*-orbitals  $(3d^8)$ .

# CONCEPT APPLICATION EXERCISE 6.1

1. **a.** Explain why  $Mn^{3+}$  is less stable than  $Mn^{2+}$  and  $Mn^{4+}$  ions?

or Explain why  $Mn^{3+}$  disproportionate into  $Mn^{2+}$  and

b. Standard reduction potential of copper is greater than that of hydrogen yet it liberates hydrogen from a concentrated solution of hydrochloric acid. Explain this fact with proper reasoning.

this fact with proper terms  $E^{\ominus}_{Cu^{2+}/Cu} = 0.34 \text{ volt}$  $2H^{\oplus} + 2e \longrightarrow H_{2(g)} \quad E^{\ominus}_{H^{\oplus}/H_{2}} = 0.00 \text{ volt}$ 

- c. An aqueous solution of FeCl<sub>3</sub> is slightly yellowish in colour.
- d. Cu(I) compounds are not known in aqueous solution
- 2. a. Write down the names of crystal structures in which the following elements are present:

  Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn
  - b. Which is more basic?
     i. ZrO<sub>2</sub> or TiO<sub>2</sub> ii. V<sub>2</sub>O<sub>5</sub> or Nb<sub>2</sub>O<sub>5</sub> iii. OsO<sub>4</sub> or ReO<sub>2</sub>
  - c. Which is more oxidising agent Cr(VI) or Mo(VI)?
- 3. Write down the name of catalyst for the following:
  - In the synthesis of hydrocarbon in Fischer–Tropsch process.
  - ii. Adams catalyst in reduction.
  - iii. Deacon's process of making Cl<sub>2</sub> from HCl.
  - iv. Reppe synthesis of benzene.
  - v. Fenton's reagent in the synthesis of aldehydes from alcohols.
- a. Arrange the following complexes in decreasing order of magnetic moment: [Ni(H<sub>2</sub>O)<sub>4</sub>]<sup>2+</sup>, [Ni(CN)<sub>4</sub>]<sup>2-</sup>, [Fe(CN)<sub>6</sub>]<sup>3-</sup>, [Fe(CN)<sub>6</sub>]<sup>4</sup>
  - **b.** Give the formula of three ions which are coloured due to charge transfer spectra.
- 5. What happen when:
  - **a.** CO<sub>2</sub> gas is passed through aqueous solution of Na<sub>2</sub>CrO<sub>4</sub>.
  - **b.** Ammonium dichromate is heated strongly.
  - c. Two gases 'A' and 'B' turns acidified K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> green. When these gases are passed through water simultaneously, solution turns turbid yellow. What are the gases 'A' and 'B'?
- 6. Explain by giving suitable reason.
  - a. Yellow coloured aqueous solution of sodium chromate changes to orange-red when CO<sub>2</sub> under pressure is passed.
  - b. Green solution of potassium manganate, K<sub>2</sub>MnO<sub>4</sub>, turns purple when CO<sub>2</sub> is circulated.
  - turns purple when  $CO_2$  is circulated. c.  $Hg^{2+}$  and  $Hg_2^{2+}$  salts are colourless.
  - d. Cu<sup>2+</sup> salts are paramagnetic while Cu<sup>⊕</sup> salts are diamagnetic in nature.
- 7. Explain:
  - **a.** Why is K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> generally preferred to Na<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> in volumetric analysis?

- b. Which divalent metal ion has maximum paramagnetic character among the first transition metals? Why?
- c. How the colour of K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> solution does depend on pH of the solution?
- Why do second and third rows of transition elements resemble each other more closely than the first row? Give reasons:
- b. Most transition metals show paramagnetic behaviours.
- c. Transition metal and their many compounds are coloured.
- 9. Acidified K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> solution turns green when sodium sulphite is added to it. Explain.
- 10. Identify A, B, C, D and X.

When a white crystalline compound X is heated with  $K_2Cr_2O_7$  and concentrated  $H_2SO_4$ , a reddish brown gas A is evolved. On passing A into caustic soda solution, a yellow coloured solution of B is obtained. Neutralising the solution of B with acetic acid and on subsequent addition of lead acetate, a yellow precipitate C is obtained. When X is heated with NaOH solution, a colourless gas is evolved and on passing this gas into  $K_2HgI_4$  solution, a reddish brown precipitate D is formed.

11. Complete and balance the following equations:

i. 
$$K_2Cr_2O_7 + \cdots + 4H_2SO_4 \longrightarrow K_2SO_4 + Cr_2(SO_4)_3 + 7H_2O + 3I_2$$

ii. 
$$K_2Cr_2O_7 \xrightarrow{\Delta} 400^{\circ}C$$

iii. KMnO<sub>4</sub> 
$$\xrightarrow{\Delta}$$
  $\xrightarrow{200^{\circ}\text{C}}$ 

iv. 
$$MnO_4^{\ominus} + AsO_3^{\ominus} + H^{\oplus} \longrightarrow$$

v. 
$$K_2Cr_2O_7 + \xrightarrow{NH_4Cl} \xrightarrow{\Delta} (Gas) + (Green)$$

$$(Metal) + (Oxide) \xleftarrow{Al}$$

- 12. Explain the following giving suitable reason:
  - a. Transition metals of 3*d*-series do not react readily with dilute acids to liberate hydrogen although they have high negative reduction potential values. Explain.
  - b. The atomic radii of the elements in a transition series do not vary much while they do vary in the case of *s* and *p*-block elements. Explain.
  - c. The second and third members in each group of the transition elements have similar atomic radii. Explain.

# COMPOUNDS AND ALLOYS OF TRANSITION METALS

# Compounds of iron, cobalt and nickel groups:

8	Group 9	Group 10	
	Co		Ferrous metals
	Rh	是 出版 不	Less occurring platinum metals
	Ir		More occurring platinum metals

These nine elements earlier made up of Group VIII in the old Mendeleev periodic table. The horizontal similarities between these elements are greater than anywhere else in the periodic table. Fe, Co and Ni are together called 'Ferrous metals' and Ru, Rh, Pd, Os, Ir, Pt are known as 'platinum metals'.

# 6.27.1 IRON AND ITS COMPOUNDS

Fe is a silvery metal which is not very hard and quite reactive. It is used in large quantities in steel making. Its biological importance is as an electron carrier in plants and animals, as haemoglobin in mammals, as nitrogenase to fix bacteria and many more. Fe is strongly ferromagnetic but the ferromagnetism is lost above the Curie temperature which is 700°C for Fe.

Iron is passivated by strong oxidising agents like conc.  $HNO_3$ ,  $K_2Cr_2O_7$  due to the formation of a protective coat of oxide  $(Fe_2O_3)$  while with dilute acids Fe is oxidised to  $Fe^{2^+}$ . Finely divided iron combines with the ligand CO forming  $[Fe(CO)_5]$  which is liquid at room temperature.

Rusting of iron is a special case of corrosion and is of great importance. Rusting occurs in the presence of  $O_2$ ,  $H_2O$  and  $H^\oplus$  due to the formation of an oxide film of  $Fe_2O_3$  which is not protective and the corrosion continues. To prevent corrosion,  $O_2$  and  $H_2O$  must be excluded. This is done by electroplating Fe with a thin layer of Sn (tin plating), dipping the Fe in molten zinc (hot dipping), electroplating with Zn (galvanising) or painting with red lead.

+2 O.S. of Fe is more stable and salts are called ferrous salts. In aqueous solutions, ferrous salts are pale green and contain the  $[Fe(H_2O)_6]^{2+}$  ion.

# 6.27.2 FERROUS SULPHATE [FeSO<sub>4</sub>·7H<sub>2</sub>O] (GREEN VITRIOL)

#### **Preparation:**

1. 
$$FeCO_3 + H_2SO_4 \longrightarrow FeSO_4 + H_2O + CO_2$$

2. FeS + 
$$H_2SO_4 \longrightarrow FeSO_4 + H_2S$$
 (Kipp's apparatus)

3. 
$$2\text{FeS}_2 + 2\text{H}_2\text{O} + 7\text{O}_2 \longrightarrow \text{FeSO}_4 + 2\text{H}_2\text{SO}_4$$

4. Fe + 
$$H_2SO_4(dil.) \longrightarrow FeSO_4 + H_2$$

#### **Properties:**

- 1. It is a pale green crystalline solid, soluble in water.
- 2. It is an efflorescent substance, and is isomorphous with Epson salt (MgSO<sub>4</sub>·7H<sub>2</sub>O) and white vitriol (ZnSO<sub>4</sub>·7H<sub>2</sub>O).
- **3.** It turns brown due to oxidation into the ferric compounds by atmospheric oxygen.

i. 
$$\operatorname{FeSO}_4 \cdot 7\operatorname{H}_2\operatorname{O} \xrightarrow{140^{\circ}\operatorname{C}} \operatorname{FeSO}_4 \cdot \operatorname{H}_2\operatorname{O} \xrightarrow{300^{\circ}\operatorname{C}} \operatorname{FeSO}_4$$
  
 $2\operatorname{FeSO}_4 \xrightarrow{\Delta} \operatorname{Fe}_2\operatorname{O}_3 + \operatorname{SO}_2 + \operatorname{SO}_3$ 

ii. 
$$Cr_2O_7^{2-} + 14H^{\oplus} + 6Fe^{2+} \longrightarrow 2Cr^{3+} + 6Fe^{3+} + 7H_2O$$

iii. 
$$MnO_4^{\ominus} + 5Fe^{2+} + 8H^{\oplus} \longrightarrow Mn^{2+} + 5Fe^{3+} + 4H_2O$$

iv. 
$$6\text{FeSO}_4 + 3\text{H}_2\text{SO}_4 + 2\text{HNO}_3 \longrightarrow 3\text{Fe}_2(\text{SO}_4)_3 + 4\text{H}_2\text{O} + 2\text{NO}$$

v. 
$$FeSO_4 + 2KCN \longrightarrow Fe(CN)_2 + K_2SO_4$$

$$Fe(CN)_2 + 4KCN \longrightarrow K_4[Fe(CN)_6]$$
(Potassium ferrocyanide)

vi. 
$$FeSO_4 + (NH_4)_2SO_4 + 6H_2O \longrightarrow FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$$

Mohr's salt

#### Uses:

- 1. It is used in the preparation of writing ink, Mohr's salt and in the extraction of gold.
- 2. It is used as laboratory reagent and as a mordant in dyeing.

# 6.27.3 FERROUS OXIDE (FeO)

It is a black powder, basic in nature and reacts with dilute acids to give  $Fe^{2+}$  salts.

$$FeO + H_2SO_4 \longrightarrow FeSO_4 + H_2O$$

It is used in glass industry to impart green colour to glass.

# 6.27.4 FERROUS OXIDE (Fe<sub>2</sub>O<sub>3</sub>) OR JEWELLER'S ROUGE

## Preparation:

- 1.  $2\text{FeSO}_4 \xrightarrow{\Delta} \text{Fe}_2\text{O}_3 + \text{SO}_2 + \text{SO}_3$  (Lab. Method)
- 2.  $4\text{FeS} + 7\text{O}_2 \longrightarrow 2\text{Fe}_2\text{O}_3 + 4\text{SO}_2$
- 3.  $2\text{Fe}(\text{OH})_3 \xrightarrow{\Delta} \text{Fe}_2\text{O}_3 + 3\text{H}_2\text{O}$

## **Properties:**

It is in the form of red powder, insoluble in water and liberates oxygen when heated at 1300°C.

1. 
$$6\text{Fe}_2\text{O}_3 \xrightarrow{1300^\circ\text{C}} 4\text{Fe}_3\text{O}_4 + \text{O}_2$$

2. 
$$Fe_2O_3 + 2NaOH \xrightarrow{Fusion} 2NaFeO_2 + H_2O$$
  
 $Fe_2O_3 + Na_2CO_3 \longrightarrow 2NaFeO_2 + CO_2$   
(Amphoteric in nature)

3. It is reduced to Fe as:

$$Fe_2O_3 + 3C \longrightarrow 2Fe + 3CO$$

$$Fe_2O_3 + 3H_2 \longrightarrow 2Fe + 3H_2O$$

$$Fe_2O_3 + 3CO \longrightarrow 2Fe + 3CO_2$$

4.  $Fe_2O_3 + 6HCl \longrightarrow 2FeCl_3 + 3H_2O$ 

#### Uses:

- 1. It is used as a red pigment.
- 2. It is used as a catalytic agent for oxidation of CO to  ${\rm CO}_2$  in Bosch Process.
- 3. A finely powdered form of Fe<sub>2</sub>O<sub>3</sub> is called Jeweller's rouge. It is used for polishing jewellery.

## 6.27.5 FERROSOFERRIC OXIDE ( $Fe_3O_a$ )

It is a mixed oxide of FeO and Fe<sub>2</sub>O<sub>3</sub>. It is more stable than FeO and Fe<sub>2</sub>O<sub>3</sub>, magnetic in nature and dissolves in acids giving a mixture of Fe<sup>2+</sup> and Fe<sup>3+</sup> salts.

$$Fe_3O_4 + 4H_2SO_4 \longrightarrow FeSO_4 + Fe_2(SO_4)_3 + 4H_2O_4$$

## 6.27.6 FERROUS SULPHIDE (FeS)

It is prepared by heating Fe filling with S. With dilute  $H_2SO_4$ , it gives  $H_2S$ .

$$FeS + H_2SO_{4(dil)} \longrightarrow FeSO_4 + H_2S_{(g)}$$

# 6.27.7 MOHR'S SALT (FeSO<sub>4</sub>(NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>·6H<sub>2</sub>O)

It is prepared from  $FeSO_4$  and  $(NH_4)_2SO_4$  and is known as  $fer_{TOly}$  ammonium sulphate and is a light green coloured double salt.  $(NH_4)_2SO_4 + FeSO_4 + 6H_2O \longrightarrow FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$ 

# 6.27.8 FERRIC CHLORIDE (FeCl<sub>3</sub>)

## Preparation:

- 1.  $2\text{Fe} + 3\text{Cl}_2 \longrightarrow 2\text{FeCl}_3$  (Anhydrous)
- 2. Hydrated FeCl<sub>3</sub>·6H<sub>2</sub>O can be prepared by dissolving ir<sub>0ħ</sub> in aqua regia or iron oxide in hydrochloric acid then by crystallising the solution.

$$2\text{Fe} + 4\text{HCl} + \text{Cl}_2 \longrightarrow 2\text{FeCl}_3 + 2\text{H}_2$$
  
 $\text{Fe}_2\text{O}_3 + 6\text{HCl} \longrightarrow 2\text{FeCl}_3 + 3\text{H}_2\text{O}$ 

## **Properties:**

- 1. Hydrated FeCl<sub>3</sub>·6H<sub>2</sub>O is yellow deliquescent crystalline solid, soluble in water, alcohol and ether, whereas anhydrous FeCl<sub>3</sub> is dark solid.
- 2. It forms addition compounds like

i. 
$$FeCl_3 + 3H_2O \longrightarrow Fe(OH)_3 + 3HCl$$

$$2\text{FeCl}_3 \xrightarrow{\Delta} 2\text{FeCl}_2 + \text{Cl}_2$$

iii. 
$$4 \text{FeCl}_3 + 3 \text{K}_4 [\text{Fe}(\text{CN})_6] \longrightarrow \text{Fe}_4 [\text{Fe}(\text{CN})_6]_3 + 12 \text{HCl}$$
  
Ferri ferro cyanide (Prussian blue)

iv. 
$$2\text{FeCl}_3 + \text{H}_2\text{S} \longrightarrow 2\text{FeCl}_2 + 2\text{HCl} + \text{S (Oxidising)}$$

v. Oxidising action:

$$2 \text{FeCl}_3 + \text{SO}_2 + 2 \text{H}_2 \text{O} \longrightarrow 2 \text{FeCl}_2 + \text{H}_2 \text{SO}_4 + 2 \text{HCl}_2 + 2 \text{FeCl}_3 + 2 \text{SnCl}_2 \longrightarrow 2 \text{FeCl}_2 + 2 \text{SnCl}_4$$

#### Uses:

- 1. It is used in medicine as disinfectant.
- 2. It is used in medicine to stop bleeding as it coagulates.
- 3. It is used in laboratory as a reagent (oxidising).

Thermal decomposition of FeC<sub>2</sub>O<sub>4</sub>:

$$F_2C_2O_4 \xrightarrow{\Delta} FeO + CO + CO_2$$

# 6.28 CYANIDE COMPLEX OF IRON

Iron forms two important complexes with the cyanide ion namely hexacyanoferrate (II)  $\{[Fe^{2+}(CN)_6]^{4-}\}$  and hexacyanoferrate(III)  $[Fe^{3+}(CN)_6]^{3-}\}$ . Hexacyanoferrate(II) is also known as ferrocyanide ion while hexacyanoferrate(III) is also known as ferricyanide ion. Both these ions form coloured salts with metal ions like  $K^{\oplus}$ ,  $Cu^{2+}$ ,  $Fe^{2+}$  which are used in qualitative analysis. Potassium ferrocyanide  $K_4[FeCN)_6]$  is a yellow coloured solid which is famously used to detect  $Fe^{2+}$  (and  $Fe^{3+}$ ) ions in solution. It forms a white coloured precipitate with  $Fe^{2+}$  and a Prussium blue solution with  $Fe^{3+}$  ions. Potassium ferricyanide  $K_3[Fe(CN)_6]$  can also be used for the same purpose as it gives Turnbulls blue colour with  $Fe^{2+}$  and a brown colour with  $Fe^{3+}$ . The reactions are:

Ferro terricyanide (Tur  

$$3^{k} + 3K_{4}[Fe(CN)_{6}] \longrightarrow Fe_{4} [Fe(CN)_{6}]_{3}$$
  
Ferri ferrocyanide (Pru

Ferri ferrocyanide (Prussian Blue)

Ferri ferricyanide (Brown)

months best tests for Fe<sup>+3</sup> is to add aqueous solutions containing lins. A blood red colour is produced due to a mixture of  $_{\rm RSCN}$ , and  $[{\rm Fe(SCN)(H_2O)_5}]^{2+}$ .

<sub>Prussian</sub> blue:

(i) It can also be represented as  $K^{\oplus}[Fe\ Fe(CN)_6]$  (potassium ferric ferro hexacyanide) (I) in addition to Fe<sub>4</sub> [Fe (CN)<sub>6</sub>]<sub>3</sub> (II). I and II are prepared as:

$$\frac{^{+3}}{\text{Fe}} + [Fe (CN)_{6}]^{4-} \longrightarrow [Fe^{3+} \{Fe^{2+} (CN)_{6}\}]^{\odot} 
(I)$$

$$\frac{^{+3}}{^{4}\text{Fe}} + 3[Fe (CN)_{6}]^{4-} \longrightarrow Fe_{4}^{3+} [Fe^{2+} (CN)_{6}]_{3}$$
(II)

Prussian blue (I) is used as a dye for blue print paper, for ink and as a bluing agent in laundry industry.

Prussian blue (II) is used as a permanent blue pigment which has great covering power.

- (ii) When FeCl<sub>3</sub> solution is added to K<sub>4</sub>[Fe(CN)<sub>6</sub>] solution, in addition to  $[Fe^{3+}\{Fe^{+2}(CN)_6\}]^{\ominus}$ ,  $[Fe^{+2}\{Fe^{+3}(CN)_6\}]^{\ominus}$  is also formed due to side redox reaction.
- (iii) When (I) is oxidised by Cl<sub>2</sub> or HNO<sub>3</sub>, it gives a green pigment, called Berlingreen (ferri ferri cyanide is obtained)  $2KFe^{3+}[Fe^{+2}(CN)_6] + Cl_2 \longrightarrow 2K + Fe^{+3}[Fe^{+3}(CN)_6]$
- (IV) With alkali, it gets decomposed to form K<sub>4</sub>[Fe(CN)<sub>6</sub>] and a brown precipitate of Fe(OH)<sub>3</sub>

 $KFe[Fe(CN)_6] + 3KOH \longrightarrow K_4[Fe(CN)_6] + Fe(OH)_3$ 

 $^{(v)}$  [Fe<sup>+3</sup> {Fe<sup>+2</sup> (CN<sup>-6</sup>)<sub>6</sub>}] $^{\odot}$  is diamagnetic.

# Turnbulls Blue:

(i) It can also be represented as  $K^{\oplus}[Fe^{+2}\{Fe^{+3}(CN)_6\}]^{\ominus}$ (potassium ferro ferric hexacyanide) (III) in addition to  $^{\text{Fe}_3^{+2}}[\text{Fe}^{+3}(\text{CN}^{-6})_6]_4 \text{ (iv)}$ 

(III) and (IV) are prepared as:

$$Fe^{+2} + [Fe^{+3}(CN)_6]^{3-} \longrightarrow [Fe^{+2} \{Fe^{+3}(CN)_6\}]^{\odot}$$
(III)

$$^{3}\text{Fe}^{+2} + 4[\text{Fe}^{+3}(\text{CN})_{6}]^{3-} \longrightarrow \text{Fe}_{3}^{+2}[\text{Fe}^{+3}(\text{CN})_{6}]_{2}$$

When  $FeCl_2$  solution is added to  $K_3[Fe(CN)_6]$  solution, in  $^{[Fe^{+2}\{Fe^{+3}(CN)_{6}\}]^{\ominus},\,[Fe^{+3}\{Fe^{+2}(CN)_{6}\}]^{\ominus}}$ 

is also obtained due to side redox reaction.

- (iii)  $[Fe^{+2}\{Fe^{+3}(CN)_6\}]^{\odot}$  is paramagnetic.
- (iv) Blue colour of Turnbull's blue is less intense than blue colour of prussian blue.

## ILLUSTRATION 6.18

A hydrated metallic salt A, light green in colour, gives a white anhydrous residue B after being heated gradually. B is soluble in water and its aqueous solution reacts with NO to give a dark brown compound C. B on strong heating gives a brown residue D and a mixture of two gases E and F. The gaseous mixture, when passed through acidified KMnO4 discharges the pink colour, when passed through acidified BaCl, solution, gives a white precipitate. Identify A, B, C, D, E and F

FeSO<sub>4</sub>·7H<sub>2</sub>O(A) 
$$\xrightarrow{\Delta}$$
 FeSO<sub>4</sub> (B) (White)  
FeSO<sub>4</sub> + NO  $\xrightarrow{H_2O}$  [Fe(H<sub>2</sub>O)<sub>5</sub> NO]SO<sub>4</sub>(C)  
FeSO<sub>4</sub>  $\xrightarrow{\Delta}$  Fe<sub>2</sub>SO<sub>3</sub>(D) + SO<sub>2</sub>(E) + SO<sub>3</sub>(F)  
SO<sub>2</sub> + SO<sub>3</sub> + KMnO<sub>4</sub>  $\longrightarrow$  Mn<sup>2+</sup>(Pink solution)  
SO<sub>2</sub> + SO<sub>3</sub> + BaCl<sub>2</sub>  $\longrightarrow$  BaSO<sub>4</sub> (White precipitate)

## ILLUSTRATION 6.19

Which of the following statements is correct?

- a. Nickel is a silver white metal.
- b. Nickel dimethylglyoxime is square planar.
- c. Among complexes of cobalt the most stable are those of  $Co^{2+}$ .
- d. Among simple compounds of cobalt the most stable are those of Co<sup>2+</sup>.

## Sol. a, b, d

Co<sup>2+</sup> state is stable in simple compounds of cobalt while the +3 state is more stable in complexes.

## ILLUSTRATION 6.20

Which of the following statement(s) is(are) correct with reference to the ferrous and ferric ions?

- a. Fe<sup>3+</sup> gives brown colour with potassium ferricyanide.
- b. Fe<sup>2+</sup> gives blue precipitate with potassium ferricyanide.
- c. Fe<sup>2+</sup> gives red colour with potassium thiocyanate.
- **d.** Fe<sup>2+</sup> gives brown colour with ammonium thiocyanate.

**Sol b**, **c** 
$$Fe^{2^+} + K_3[Fe(CN)_6] \longrightarrow Fe_3^{11} [Fe^{111}(CN)_6] \downarrow$$
Ferro ferricyanide (Turnbulls Blue)
$$Fe^{3^+} + K(SCN) \longrightarrow Fe(SCN)_3 \downarrow \text{ (Blood red)}$$

## 6.29 COBALT AND ITS COMPOUNDS

Cobalt is a very tough metal which resembles iron. It is bluish white and lustrous in appearance. Like iron it is ferromagnetic (Curie temperature = 1000°C) but relatively unreactive as it does not react with H<sub>2</sub>O, H<sub>2</sub> or N<sub>2</sub>. However, it forms the most number of complexes and more compounds than any other element except carbon.

## 6.29.1 Co<sup>2+</sup> STATE

+II state is the most important oxidation state for simple compounds of cobalt. Some compounds in this state are CoO, CoCl<sub>3</sub>, CoSO<sub>4</sub>, CoCO<sub>3</sub>. The hydrated salts are all pink or red due to the hexahydrate ion  $[Co(H_2O)_6]^{2+}$  while CoO is olive green. Thus CoCl, is used as a test for water and as an indicator added to the drying agent 'silica gel'. CoO in combination with ZnO is used as a green pigment in paints called Rinnmann's green.

## 6.29.2 Co3+ STATE

+III state is the most important state for complexes of cobalt. Since the (+II) state is common for simple compounds, it is difficult to oxidise Co<sup>2+</sup> to Co<sup>3+</sup> and Co<sup>3+</sup> are less stable and are reduced by water. In contrast many Co(+II) complexes are readily oxidised to Co(+III) complexes, Co(+III) complexes being more stable.

## 6.30 NICKEL AND ITS COMPOUNDS

Nickel, a silvery white metal which does not tarnish in air is produced in large quantities and used in a wide variety of alloys both ferrous and non-ferrous. All three metals (Ni, Pd, Pt) of Group 10 are used as catalysts in many reactions. For example, 'Raney Nickel' is very finely divided nickel used in reduction processes and Pd is used for hydrogenation.

Nickel is predominantly divalent in both its simple compounds and complexes. The hydrated salts are bright green coloured due to the hydrated ion [Ni(H2O)6]2+. Complexes are commonly square planar or octahedral. The red coloured complex precipitated by Ni<sup>2+</sup> and dimethylglyoxime from slightly ammonical solution is square planar. This reaction is used both for detection and quantitative estimation of Ni.

## 6.31 COPPER

## 6.31.1 PROPERTIES OF COPPER

- 1. It is a reddish coloured lustrous metal, soil, malleable and ductile and is the best conductor next to silver.
- 2. Molten metal adsorbs (occludes)  $SO_2$  gas which is given off on heating.
- 3. Non-oxidising acids HCl and dil.  $H_2SO_4$  do not have any effect on copper. However they dissolve copper in the presence of air.

$$2Cu + 4HCl (dil.) + O_2 \longrightarrow 2CuCl_2 + 2H_2O$$

$$6Cu + 6HCl (conc.) + 3O_2 \longrightarrow 3CuCl_2 \cdot 3Cu(OH)_2$$
Atacamite

$$2\text{Cu} + 2\text{H}_2\text{SO}_4 \text{ (dil.)} + \text{O}_2 \longrightarrow 2\text{CuSO}_4 + 2\text{H}_2\text{O}$$

$$\text{Cu} + 2\text{H}_2\text{SO}_4 \text{ (conc.)} \longrightarrow \text{CuSO}_4 + \text{SO}_2 + 2\text{H}_2\text{O}$$

**4.** Cu reacts with SO<sub>2</sub> in air.

$$8Cu + 6H2O + 2SO2 + 5O2 \longrightarrow 2[CuSO4·3Cu(OH)2]$$
Bronchantite

5. It produces green coating of basic copper carbonate [CuCO<sub>3</sub>.  $Cu(OH)_2$ ] in presence of moisture and  $CO_2$  in air  $(O_2)$ . It is also known as Copper Patina or Verdigris.

$$2\mathsf{Cu} + \mathsf{H}_2\mathsf{O} + \mathsf{CO}_2 + \mathsf{O}_2 \longrightarrow \mathsf{CuCO}_3 \cdot \mathsf{Cu}(\mathsf{OH})_2$$

- 6. Dissolves in NH<sub>4</sub>OH solution in the presence of air. Dissolves in 304  $\longrightarrow 2[Cu(NH_3)_4(OH)_2](B|_{Ue_3})$ Cupra ammonium complex
- 7. Copper reduces oxides of nitrogen to elementary nitrogen

$$2Cu + 2NO \longrightarrow 2CuO + N_2$$

$$Cu + 2Fe^{3+} \longrightarrow Cu^{2+} + 2Fe^{2+}$$

The etching of designs on copper plates using ferric chloride.

$$2FeCl_3 + Cu \longrightarrow CuCl_2 + 2FeCl_2$$

8. Nitric acid reacts with Cu as follows:

$$3\text{Cu} + 8\text{HNO}_3(\text{dil.}) \longrightarrow 3\text{Cu}(\text{NO}_3)_2 + 4\text{H}_2\text{O} + 2\text{NO}_3(\text{Cu} + 4\text{HNO}_3(\text{conc.})) \longrightarrow \text{Cu}(\text{NO}_3)_2 + 2\text{H}_2\text{O} + 2\text{NO}_3(\text{Cu} + 2\text{NO}_3)_3 + 2\text{H}_2\text{O} + 2\text{NO}_3(\text{Cu} +$$

9. When heated in oxygen (air), it forms two oxides as  $f_{0||_{0}y_0}$ 

$$2Cu + O_2 \xrightarrow{<1100^{\circ}C} 2CuO$$

$$Cupric oxide$$

$$4Cu + O_2 \xrightarrow{>1100^{\circ}C} 2Cu_2O$$

$$Cuprous oxide$$
(Red)

#### 6.31.2 USES OF COPPER

- 1. Copper is the second most useful metal (first being iron) because of its stability in air and water having excellent conductivity and thus is used in the manufacture of electrical wires, cables etc.
- 2. It is used for electroplating and electrotyping.
- 3. It is used for making vacuum pumps, calorimeter, steam boilers, kettles etc.
- 4. It is used in the manufacture of coins, copper salts and in de-silverisation of lead.

## 6.31.3 ALLOYS OF COPPER

Alloys	Composition	Alloy	Composition
Brass	60% Cu + 40% Zn	German	56% Cu + 24%
12/11/20		silver	$Z_n + 20\% N_i$
Gun-metal	90% Cu + 8% Sn +	Manganin	86-78% Cu+
	2% Zn		13-18% Mn -
			1-4% Ni
Bronze	75-90% Cu +	Bell metal	80% Cu - 20%
	10–25% Sn		20% Sn
Aluminium	90% Cu + 10% Al	Constantan	60% Cu + 40%
bronze			Ni
Monel metal	30% Cu + 67% Ni		
	+ 3% (Fe + Mn)		

# 6.32 COMPOUNDS OF COPPER

## 6.32.1 COPPER SULPHATE [CuSO<sub>4</sub>·5H<sub>2</sub>O] (BLUE VITRIOL)

## **Preparation:**

- 1.  $CuCO_3 \cdot Cu(OH)_2 + 2H_2SO_4 \longrightarrow 2CuSO_4 + 3H_2O + CO_2$
- 2.  $CuO + H_2SO_4 \longrightarrow CuSO_4 + H_2O$
- 3.  $CuFeS_2 + 4O_2 \longrightarrow CuSO_4 + FeSO_4$
- 4.  $2Cu + 2H_2SO_4 + O_2 \longrightarrow 2CuSO_4 + 2H_2O$

blue coloured crystalline solid, fairly soluble in When heated slowly, it decomposes in the following stages:

$$CuO + SO_3 \leftarrow \frac{673 \text{ K}}{CuSO_4}$$

Aphlydrous CuSO<sub>4</sub> regains its blue colour when moistened with a drop of water. (Test of presence of water)

$$\underset{\text{vith a drop of water}}{\text{with a drop of water}} \stackrel{\text{750°C}}{\Delta} \rightarrow 2\text{CuO} + 2\text{SO}_2 + \text{O}_2$$

(extremely poisonous)

$$_{(uCN + KCN(excess))} \longrightarrow K_3[Cu(CN)_4] (Complex)$$

$$(uCN + RCH(excess)) = (Cu(OH)_2 + (NH_4)_2SO_4 + (2NH_4OH) \longrightarrow (Cu(OH)_2) + (NH_4)_2SO_4 + (NH_4OH) \longrightarrow (Cu(OH)_2) + (NH_4OH) \longrightarrow$$

$$\begin{array}{c} \text{Cu(OH)}_2 + 2\text{NH}_4\text{OH} \longrightarrow \left[\text{Cu(NH}_3)_4\right] (\text{OH)}_2 + 4\text{H}_2\text{O} \end{array}$$

$$(u(OH)_2 + OH_4OH \longrightarrow [Cu(NH_3)_4](OH)_2 + (NH_4)_2SO_4$$

When dilute solution of CuSO<sub>4</sub> is treated with KSCN (potassium thiocyanate) and SO<sub>2</sub> gas is bubbled through it, cuprous thiocyanate is precipitated.

$$2\text{CuSO}_4 + 2\text{KSCN} + \text{SO}_2 + 2\text{H}_2\text{O} \longrightarrow 2\text{CuSCN} + \text{K}_2\text{SO}_4 + 2\text{H}_2\text{SO}_4$$

$$\text{\& 2CuSO}_4 + 4\text{KI} \longrightarrow \text{Cu}_2 \text{I}_2 + \text{I}_2 + 2\text{K}_2 \text{SO}_4$$

(CuI is not formed)

Litis largely employed in electroplating, electric batteries.

- 1 It is used as a mordent for dyeing, calico printing, germ killer and fungicide.
- 3. It is used in medicine as antiseptic, laboratory reagent for green pigments.
- 4. It is used in making Fehling's solution and making Bordeaux mixture: [CuSO<sub>4</sub> + Lime (milk lime)] used for dusting vines, trees, potatoes to kill fungi and moulds.

# <sup>∫33,2</sup> CUPRIC CHLORIDE [CuCl<sub>2</sub>·2H<sub>2</sub>O]

httparation: The metal or cupric oxide or cupric hydroxide or mer carbonate is dissolved in conc. HCl. The resulting solution acrystallisation gives green crystals of hydrated cupric chloride.

$$^{1,2C_{U}+4HCl} + O_{2} \longrightarrow 2CuCl_{2} + 2H_{2}O$$

$$CuO + 2HCl \longrightarrow CuCl_2 + H_2O$$

$$^{2\text{Cu(OH)}_{2}\text{\cdot}\text{CuCO}_{3}+4\text{HCl}} \longrightarrow ^{2} ^{2\text{CuCl}_{2}+3\text{H}_{2}\text{O}+\text{CO}_{2}}$$

Anhydrous cupric chloride is obtained as a dark brown mass when copper metal is heated in excess of chlorine gas or by heating hydrated cupric chloride in HCl gas at 150°C.

$$C_{u} + Cl_{2} \longrightarrow CuCl_{2}$$

$$\text{CuCl}_2 \cdot 2\text{H}_2\text{O} + \text{HCl}_{(g)} \xrightarrow{150^{\circ}\text{C}} \text{CuCl}_2 + 2\text{H}_2\text{O}$$

## **Properties:**

- 1. It is a deliquescent compound and is readily soluble in water. The dilute solution is blue but concentrated solution is, however, green. It changes to yellow when conc. HCl is added. The blue colour is due to complex cation [Cu(H2O)4]2+ and yellow colour due to complex anion [CuCl<sub>4</sub>]<sup>2-</sup> and green when both are present.
- 2. The aqueous solution is acidic due to its hydrolysis.

$$CuCl_2 + 2H_2O \longrightarrow Cu(OH)_2 + 2HCl$$

3. 
$$CuCl_2 + 2NaOH \longrightarrow Cu(OH)_2 + 2NaCl$$

$$CuCl_2 + 3Cu(OH)_2 \longrightarrow CuCl_2 \cdot 3Cu(OH)_2$$

4. 
$$3(CuCl_2 \cdot 2H_2O) \longrightarrow CuO + Cu_2Cl_2 + 2HCl + Cl_2 + 5H_2O$$

$$2CuCl_2 + SO_2 + 2H_2O \longrightarrow Cu_2Cl_2 + 2HCl + H_2SO_4$$

$$2CuCl_2 + SnCl_2 \longrightarrow Cu_2Cl_2 + SnCl_4$$

5. 
$$CuCl_2 + 4NH_4OH \longrightarrow Cu(NH_3)_4Cl_2 \cdot H_2O + 3H_2O$$

#### Uses:

- 1. It is used as an oxygen carrier in the preparation of organic dve stuffs.
- 2. It is used in medicines.
- 3. It is used as catalyst in Deacon's process for the preparation of Cl<sub>2</sub>.

## 6.32.3 CUPRIC OXIDE [(CuO) BLACK COPPER OXIDE]

### Preparation:

1. By heating Cu<sub>2</sub>O in air or by heating copper for a long time in air.

$$2Cu_2O + O_2 \xrightarrow{\Delta} 4CuO$$

$$2Cu + O_2 \xrightarrow{\Delta} 2CuO$$

2. By heating copper nitrate.

$$2Cu(NO_3)_2^{\circ} \xrightarrow{\Delta} 2CuO + 4NO_2 + O_2$$

3. By heating cupric hydroxide and basic copper carbonate. CuCO<sub>2</sub>·Cu(OH)<sub>2</sub>

$$Cu(OH)_2 \xrightarrow{\Delta} CuO + H_2O$$

$$CuCO_3 \cdot Cu(OH)_2 \xrightarrow{\Delta} 2CuO + H_2O + CO_2$$

#### **Properties:**

- 1. It is a black powder, stable to moderate heating.
- 2.  $CuO + 2HCl \longrightarrow CuCl_2 + H_2O$

$$CuO + H_2SO_4 \longrightarrow CuSO_4 + H_2O$$

$$CoO + 2HNO_3 \longrightarrow Cu(NO_3)_2 + H_2O$$

3. 
$$CuO + H_2 \longrightarrow Cu + H_2O$$

$$CuO + C \longrightarrow Cu + CO$$

$$CuO + CO \longrightarrow Cu + CO_2$$

4. 
$$4\text{CuO} \xrightarrow{1100-1200^{\circ}\text{C}} 2\text{Cu}_2\text{O} + \text{O}_2$$

#### Uses:

- 1. It is used to impart green and blue colour to glazes and glasses.
- 2. It is used in petroleum to remove sulphur.

## 6.32.4 Cuprous Oxide [(Cu<sub>2</sub>O) Red Copper Oxide]

In nature it occurs as cuprite known as red copper ore.

Preparation: It may be prepared by any one of the following methods:

- 1.  $CuO + Cu \xrightarrow{Heat} Cu_2O$
- 2. Reduction of CuO or compounds or mixture containing CuSO<sub>4</sub>.

$$\begin{array}{ccc} \text{2CuO} & + & \text{Glucose} & \longrightarrow & \text{2Cu}_2\text{O} + \text{Gluconic acid} \\ \text{or Aldehyde or HCOOH} & & \text{Red ppt} \end{array}$$

$$2\text{CuSO}_4 + 2\text{Na}_2\text{CO}_3 + \text{Na}_2\text{SO}_3 \longrightarrow \text{Cu}_2\text{O} + 3\text{Na}_2\text{SO}_4 + 2\text{CO}_2$$

### **Properties:**

- 1. Red powder, insoluble in water and alkalies.
- 2. It can be oxidised to CuO by heating it in air.  $2Cu_2O + O_2 \xrightarrow{\Delta} 4CuO$
- 3. It can be reduced to copper when heated with carbon or in a current of H<sub>2</sub> or CO.

$$Cu_2O + C \longrightarrow 2Cu + CO$$

$$Cu_2O + H_2 \longrightarrow 2Cu + H_2O$$

$$Cu_2O + CO \longrightarrow 2Cu + CO_2$$

- 4. Similarly hot nitric acid is reduced by Cu<sub>2</sub>O.  $3Cu_2O + 14HNO_3(dil.) \longrightarrow 6Cu(NO_3)_2 + 7H_2O + 2NO$  $Cu_2O + 2HNO_3 \longrightarrow Cu(NO_3)_2 + H_2O + Cu$
- 5. Hot concentrated H<sub>2</sub>SO<sub>4</sub> is reduced by cuprous oxide.  $Cu_2O + 3H_2SO_4 \longrightarrow 2CuSO_4 + 3H_2O + SO_2$
- 6. Acids dissolve and decompose Cu<sub>2</sub>O to give cupric salt and copper.

$$Cu_2O + H_2SO_4 \longrightarrow CuSO_4 + Cu + H_2O$$

7. Alkali cyanides dissolve it to yield the colourless cuprocyanide complex.

$$Cu_2O + 6KCN + H_2O \longrightarrow 2K_2[Cu(CN)_3] + 2KOH$$

8. Concentrated NH<sub>4</sub>OH dissolves it to form the complex diamminecuprous hydroxide in the absence of air. In the presence of air, however, there is oxidation and diamminecupric hydroxide is formed.

$$Cu_2O + 4NH_3OH \longrightarrow 2[Cu(NH_3)_2]OH + 3H_2O$$

9. With concentrated HCl, a complex compound is formed.  $Cu_2O + 6HCl \longrightarrow 2H_2[CuCl_3] + H_2O$ 

#### Uses:

- 1. It is used in making ruby glass and enamel.
- 2. It is used in the manufacture of antirust paint.
- 3. It is used in electrical circuits as a rectifier.

## ILLUSTRATION 6.21

Hydrazine reduces Fehling's solution to form:

- a. Cu(OH),
- b. Cu<sub>2</sub>O
- c. CuO
- **d.**  $Cu + O_2$
- **Sol. b.** Fehling's test reduces CuO to red coloured Cu<sub>2</sub>O.

## ILLUSTRATION 6.22

In the following reaction, Y and Z are respectively:

$$4AgNO_3 + 2Cl_2(Dry) \longrightarrow 4X + 2Y + Z$$

**a.** AgCl, 
$$O_2$$
 **b.**  $NO_2$ ,  $N_2O_4$  **c.**  $N_2O_5$ ,  $O_2$  **d.**  $N_{one}$ 

Sol. c. 
$$4AgNO_3 + 2Cl_2 \longrightarrow 4AgCl(X) + N_2O_5(Y) + O_2(Z)$$

## ILLUSTRATION 6.23

Explain the following facts:

- a. Copper hydroxide is soluble in ammonium hydroxide but not in sodium hydroxide.
- b. Addition of an alkali to cuprous chloride solution gives a yellow precipitate which gradually changes to a red colour.

### Sol.

- a. This is because Cu<sup>2+</sup> can form many complexes with NH, which are soluble in water.
- **b.**  $Cu_2Cl_2 + 2NaOH \longrightarrow Cu_2O\downarrow + 2NaCl + H_2O$ The precipitate changes colour from yellow to red due to formation of Cu<sub>2</sub>O.

# 6.33 **ZINC**

## 6.33.1 PROPERTIES OF ZINC

- 1. It is a bluish white crystalline metal brittle at ordinary temperature.
- 2. It is malleable and ductile at 100–150°C and again becomes brittle at 220°C.
- 3. When molten zinc is poured in cold water, granulated zinc is obtained.
- 4.  $2Zn + O_2 \xrightarrow{\Delta} 2ZnO$
- 5.  $Zn + H_2O_{(g)} \longrightarrow ZnO + H_2$
- 6.  $4Zn + 3H_2O + CO_2 + 2O_2 \longrightarrow ZnCO_3 \cdot 3Zn(OH)_2$
- 7.  $Zn + 2HCl \longrightarrow ZnCl_2 + H_2$
- 8. It reacts with oxidising acids as follows.
  - i.  $Zn + 2H_2SO_4$  (conc.)  $\longrightarrow ZnSO_4 + 2H_2O + SO_2$
  - ii.  $3Zn + 4H_2SO_4$  (dil.)  $\longrightarrow 3ZnSO_4 + S + 4H_2O$
  - iii.  $4Zn + 5H_2SO_4$  (moderately conc.)  $\longrightarrow 4ZnSO_4$
  - iv.  $4Zn + 10HNO_3(\text{very dil.}) \longrightarrow 4Zn(NO_3)_2 + NH_4NO_3$
  - v.  $3Zn + 8HNO_3$  (moderately conc.)  $\longrightarrow 3Zn(NO_3)_2$
  - vi.  $Zn + 4HNO_3$  (hot conc.)  $\longrightarrow Zn(NO_3)_2 + 2NO_2$

9. Zinc dissolves in hot NaOH solution forming soluble zincate ion liberating hydrogen.

$$\frac{\text{ion liberating Hyane general}}{\text{Zn} + 2\text{NaOH}} \longrightarrow \text{Na}_2\text{ZnO}_2 + \text{H}_2$$

$$\frac{\text{Zn} + 2\text{NaOH} + 2\text{H}_2\text{O}}{\text{Zn} + 2\text{NaOH} + 2\text{H}_2\text{O}} \longrightarrow \text{Na}_2[\text{Zn(OH)}_4] + \text{H}_2$$
Sodium zincate

10. Zinc, being highly electropositive metal shows lots of electrochemical displacement reactions.

$$cusO_4 + Zn \longrightarrow ZnSO_4 + Cu$$
i.  $cusO_4 + Zn \longrightarrow ZnSO_4 + Cu$ 

i. 
$$Pb(NO_3)_2 + Zn \longrightarrow Zn(NO_3)_2 + Pb$$

# 6.33.2 USES OF ZINC

- 1. Zinc sheets are used for roofing.
- 2. Zn-dust is used as reducing agent and also in precipitation of silver and gold from their complex cyanides.
- 3. It is used in desilverisation of lead in Parke's process.
- 4. In the manufacture of Zn-Cu couple by depositing copper on zinc (dust) which reacts with water or alcohol and produces nascent hydrogen which acts as reducing agent.
- 5. It is used in the making of alloys like brass, german silver and making batteries.
- 6. It is used for galvanising iron (deposition of thin and coherent layer of Zn on iron sheets to avoid corrosion), It is achieved by dipping iron plates in molten zinc.

# 6.34 COMPOUNDS OF ZINC

## 6.34.1 ZINC OXIDE [ZnO]

#### Preparation:

1. 
$$2Zn + O_2 \longrightarrow 2ZnO$$

$$2. 3\text{Zn} + 8\text{HNO}_3 \longrightarrow 3\text{Zn(NO}_3)_2 + 4\text{H}_2\text{O} + 2\text{NO}_3$$

$$2Zn(NO_3)_2 \xrightarrow{\Delta} 2ZnO + 4NO_2 + O_2$$

3. 
$$Zn(OH)_2 \xrightarrow{\Delta} ZnO + H_2O$$

## Properties:

- 1. It is white, light powder insoluble in water and known as Philosopher's Wool. On heating it becomes yellow and on cooling it becomes white.
- 2. It is reduced to Zn by the reaction of charcoal or dry  ${\rm H}_2$ .

$$ZnO + H_2 \longrightarrow Zn + H_2O$$

$$ZnO + C \longrightarrow Zn + CO$$

3. 
$$Z_{nO} + 2NaOH \longrightarrow Na_2Z_{nO_2} + H_2O$$

4. 
$$ZnO + 2HCl \longrightarrow ZnCl_2 + H_2O$$

- 1. It is used as white paint and in the manufacture of glass and pottery glases.
- 2. It is used in medicine as zinc ointment.
- 3. It is used in xerox printing, white shoe polish, a filler for rubber.
- 4. It does not tarnish even in H, S as ZnS is also white in colour.
- 5. Mixture of ZnO and ZnCl<sub>2</sub> forms good cement for teeth.

## 6.34.2 ZINC SULPHIDE [ZnS]

#### **Preparation:**

- 1.  $ZnSO_A + H_2S \longrightarrow ZnS + H_2SO_A$
- 2.  $2ZnO + 3S \xrightarrow{\Delta} 2ZnS + SO_2$
- 3. By the reaction of ammonical solution of zinc salt and H<sub>2</sub>S.

$$ZnCl_2 + H_2S + 2NH_3 \longrightarrow ZnS + 2NH_4CI + 2H_2O$$
  
 $Na_2ZnO_2 + 2H_2S \longrightarrow ZnS + Na_2S + 2H_2O$ 

## **Properties:**

- 1. It turns yellow on exposure to light.
- 2. It is a white solid insoluble in water and acetic acid and soluble in mineral acids.
- 3. Due to impurities of sulphides of Mn, Cu, Ag, etc. it shows phosphorescence.

#### Uses:

- 1. It is used in luminous paint on watch dials (one part Ra in 10 million ZnS).
- 2. It is used as a phosphorescent.
- 3. It is used for X-ray screen in radioactive work.
- 4. It is used in white paint: Lithopone (ZnS + BaSO<sub>4</sub>).

## 6.34.3 Zinc Sulphate [ZnSO<sub>4</sub>.7H<sub>2</sub>O] (White Vitriol)

#### Preparation:

It is prepared by the action of dil.  $H_2SO_4$  on Zn metal or its oxide

$$ZnCO_3 + H_2SO_4 \longrightarrow ZnSO_4 + H_2O + CO_2$$

### **Properties:**

- 1. It is highly soluble in water.
- 2. It is isomorphous with epsom salt and green vitriol.

3. 
$$ZnSO_4 \cdot 7H_2O \xrightarrow{100^{\circ}C} ZnSO_4 \cdot 6H_2O \xrightarrow{280^{\circ}C} ZnSO_4 \xrightarrow{800^{\circ}C} ZnO + SO_2 + O_2$$

4. 
$$ZnSO_4 \xrightarrow{100^{\circ}C} ZnO + SO_3$$

#### Uses:

- 1. It is used in medicine as an eye lotion.
- 2. It is used in dyeing industry.
- 3. It is used in the manufacture of Lithopone.

# 6.34.4 ZINC CHLORIDE [ZnCl<sub>2</sub>]

## Preparation:

1. It is obtained by treating zinc oxide or zinc carbonate or zinc hydroxide with dilute HCl. The solution on concentration and cooling gives hydrated ZnCl<sub>2</sub> crystals, ZnCl<sub>2</sub>·2H<sub>2</sub>O.

$$ZnO + 2HCl \longrightarrow ZnCl_2 + H_2O$$

$$ZnCO_3 + 2HCl \longrightarrow ZnCl_2 + CO_2 + H_2O$$

$$Zn(OH)_2 + 2HCl \longrightarrow ZnCl_2 + 2H_2O$$

**2.** Anhydrous zinc chloride is obtained by heating zinc in the atmosphere of dry chloride or dry HCl gas.

$$Zn + Cl_2 \longrightarrow ZnCl_2$$
  
 $Zn + 2HCl \longrightarrow ZnCl_2 + H_2$ 

3. Anhydrous ZnCl<sub>2</sub> cannot be obtained by heating zinc chloride as on hydrolysis, basic chloride (zinc hydroxy chloride) is formed which on further heating gives zinc oxide.

$$ZnCl_2 \cdot 2H_2O \longrightarrow Zn(OH)Cl + HCl + H_2O$$
  
 $Zn(OH)Cl \longrightarrow ZnO + HCl$ 

#### **Properties:**

- 1. Anhydrous ZnCl<sub>2</sub> is white solid, deliquescent and soluble in water. It melts at 660°C and boils at 730°C.
- 2.  $ZnCl_2 \cdot 2H_2O \longrightarrow Zn(OH)Cl + HCl + H_2O$   $2(ZnCl_2 \cdot 2H_2O) \longrightarrow Zn_2OCl_2 + 2HCl + 3H_2O$ Zinc oxychloride
- 3.  $ZnCl_2 + H_2S \longrightarrow ZnS \downarrow + 2HCl$ White precipitate
- 4.  $ZnCl_2 + 2NH_4OH \longrightarrow Zn(OH)_2 + 2NH_4Cl$   $Zn(OH)_2 + 2NH_4OH + 2NH_4Cl \longrightarrow [Zn(NH_3)_4]Cl_2 + 4H_2O$ Tetraminezinc chloride
- 5.  $ZnCl_2 + 2NaOH \longrightarrow Zn(OH)_2 + 2NaCl$   $Zn(OH)_2 + 2NaOH \longrightarrow Na_2ZnO_2 + 2H_2O$ Sodium zincate
- 6.  $ZnCl_2 + 4NH_3 \longrightarrow ZnCl_2 \cdot 4NH_3$
- 7. Its syrupy solution when mixed with zinc oxide. ZnO sets to a hard mass forming an oxychloride, ZnCl<sub>2</sub>·3ZnO.
- 8.  $4ZnCl_2 + 4Na_2CO_3 + 3H_2O \longrightarrow ZnCO_3 \cdot 3Zn(OH)_2$ Basic zinc carbonate  $+ 8NaCl + 3CO_2$

$$ZnCl_2 + 2NaHCO_3 \longrightarrow ZnCO_3 + 2NaCl + H_2O + CO_2$$

9. Thermal decomposition of  $Zn(NO_3)_2$ .

$$Zn(NO_3)_2 \xrightarrow{\Delta} ZnO + 2NO_2 + \frac{1}{2}O_2$$

#### Uses:

- 1. It is used as dehydrating agent.
- 2. The concentrated solution of ZnCl<sub>2</sub> is used for impregnating timber to prevent its destruction by the action of microorganisms.
- **3.** The mixture of syrupy zinc chloride solution and zinc oxide is used for dental filling.

## 6.35 GOLD

## 6.35.1 PROPERTIES OF GOLD

- 1. Gold is a soft, heavy and yellow metal with high lustre.
- 2. It is a good conductor of heat and electricity and has a high melting and boiling points.
- 3. It is highly malleable and ductile.

4. It is not attacked by ordinary air (oxygen), water or steam. It does not displace hydrogen from acids. It is not attacked even by strong alkalies. It however dissolves in aqua regia (3 parts of conc. HCl and 1 part conc. HNO<sub>3</sub>) to give auric chloride, AuCl<sub>3</sub>.

$$2Au + 9HCl + 3HNO_3 \longrightarrow 2AuCl_3 + 6H_2O + 3NOCl$$
  
 $AuCl_3 + HCl \longrightarrow HAuCl_4$  (Chloroauric acid)

#### 6.35.2 COMPOUNDS OF GOLD

AuCl<sub>3</sub>: Gold reacts with chlorine to form chloride. It is a reddish solid soluble in H<sub>2</sub>O. It reacts with HCl to give H[AuCl<sub>4</sub>] which is used in toning process in photography. 2Au + 3Cl<sub>2</sub> → 2AuCl<sub>3</sub>

$$HCl + AuCl_3 \longrightarrow H[AuCl_4]$$

2. Au<sub>2</sub>S: It is a dark brown solid insoluble in water and is prepared as follows:

$$2K[Au(CN)_2] + H_2S \longrightarrow Au_2S + 2KCN + 2HCN$$

## 6.36 SILVER

#### 6.36.1 PROPERTIES OF SILVER

- 1. It is a lustrous white metal, which is ductile and malleable and a very good conductor of heat and electricity (better than copper).
- 2. On heating the molten mass of silver absorbs oxygen which is again released on cooling. This is called as spitting of silver.
- 3. There is no effect of air and alkalies on silver.
- 4. The air contaminated with H<sub>2</sub>S tarnishes silver due to formation of Ag,S (black).

$$4Ag + 2H_2S + O_2 \longrightarrow 2Ag_2S + 2H_2O$$

5. It dissolves in alkali cyanide.

$$4Ag + 8KCN + 2H_2O + O_2 \longrightarrow 4K[Ag(CN)_2] + 4KOH$$
Argentocyanide complex

- 6.  $3Ag + 4HNO_3(dil.) \longrightarrow 3AgNO_3 + 2H_2O + NO$  $Ag + 2HNO_3(conc.) \longrightarrow AgNO_3 + H_2O + NO_2$
- 7. Dil.  $H_2SO_4$  has no action on silver.  $2Ag + 2H_2SO_4(conc.) \longrightarrow Ag_2SO_4 + 2H_2O + SO_2$

## 6.36.2 USES OF SILVER

- 1. It is used in preparation of silver slates. It is used for photography and as conductor of electricity (the best conductor of electricity).
- 2. It is used in silver plating.
- 3. Silver leaves are used in Ayurvedic and Yunani medicines
- 4. Alloyed with Cu, it is used in making coins, jewellery and decorative articles and silver wares.
- 5. Silver amalgam is used for filling teeth.

# 6.37 COMPOUNDS OF SILVER

# 6.37.1 SILVER NITRATE [AgNO<sub>3</sub>] (LUNAR CAUSTIC) Preparation:

$$3Ag + 4HNO_3 \longrightarrow 3AgNO_3 + 2H_2O + NO$$

1. It is a colourless crystalline solid, soluble in water.

$$\frac{\Delta}{2.2 \text{AgNO}_3} \xrightarrow{\text{Red hot}} 2 \text{Ag} + 2 \text{NO}_2 + \text{O}_2 \uparrow$$

$$_{3, 2}AgNO_3 + 2NaOH \longrightarrow Ag_2O + 2NaNO_3 + H_3O$$

4. 
$$2AgNO_3$$
 above melting point  $2AgNO_2 + O_2$ 

$$AgNO_2 \xrightarrow{950 \text{ K}} Ag + NO_2$$

$$5.2 \text{AgNO}_3 + \text{BaCl}_2 \longrightarrow 2 \text{AgCl} + \text{Ba(NO}_3)_2$$

$$6. 2AgNO_3 + 2NH_4OH \longrightarrow Ag_2O + 2NH_4NO_3 + H_2O$$

$$Ag_2O + 4NH_4OH \longrightarrow 2[Ag(NH_3)_2]OH + 3H_2O$$

7. 
$$5AgNO_3 + 3H_2O + 3I_2 \text{ (excess)} \longrightarrow HIO + 5AgI + 5HNO_3$$
  
 $6AgNO_3 \text{(excess)} + 3I_2 + 3H_2O \longrightarrow AgIO_3 + 5AgI + 6HNO_3$ 

lises:

- 1. It is used in photography.
- 2. It is used in making of marking ink used for marking linen.
- 3. It is used in silvering mirrors.
- 4. It has a caustic and destructive effect of organic tissues. It produces burning sensation (like caustic) and reduces to metallic silver which is white like the lunar moon, hence the name **lunar caustic.**
- 5. In small doses it is used as a medicine in nervous diseases.

## 6.37.2 SILVER BROMIDE [AgBr]

Preparation:

$$AgNO_3 + NaBr \longrightarrow AgBr + NaNO_3$$

Properties:

- It is a pale yellow white solid, insoluble in water and conc. HNO<sub>3</sub> but soluble in excess of NH<sub>4</sub>OH.
- 2.  $AgBr + 2KCN \longrightarrow K[Ag(CN)_2] + KBr$
- 3.  $AgBr + 2Na_2S_2O_3 \longrightarrow Na_3[Ag(S_2O_3)_2] + NaBr$
- 4.  $AgBr + 2NH_4OH \longrightarrow [Ag(NH_3)_2]Br + 2H_2O$

Note:

- i AgCl, AgBr, AgI are insoluble in H<sub>2</sub>O. It is due to high lattice energy of these compounds.
- ii. AgF is soluble in  $H_2O$ . It is due to large (negative hydration enthalpy of  $F^{\odot}$  ions.).
- 5. All the silver halides (AgX) dissolve in thiosulphate ( $S_2O_3^{2-}$ ) and cyanide ( $CN^{\Theta}$ ) solution giving thiosulphato and dicyano complexes of  $Ag^{\oplus}$  ion, as shown in Figures and respectively.

$$\begin{bmatrix} \Theta_{0} & & & & \\ \Theta_{0} & & & & \\ & & & & \\ \end{bmatrix}^{S} S \begin{bmatrix} O^{\Theta} \\ O^{\Theta} \end{bmatrix}^{3-1}$$

Structure of dithiosulphato argentate(I) ion

$$\bigcirc N = C - Ag^{\oplus} - C = N^{\ominus} \bigcirc$$

## Structure of dicyanoargentate(I) ion

Uses:

1. AgBr is used in photographic films, since it is very sensitive to light.

$$2AgBr \xrightarrow{hv} 2Ag + Br_2$$

2. Recovery of Ag and Cu from its alloy:

$$(Ag + Cu) \xrightarrow{\text{dil. HNO}_3} AgNO_3 + Cu(NO_3)_2 \xrightarrow{250^{\circ}C} AgNO_3 + CuO$$

AgNO<sub>3</sub> and CuO are washed in water. CuO is obtained as residue and the filtrate contains AgNO<sub>3</sub>. The filtrate is heated strongly to give silver (Ag).

$$2AgNO_3 \longrightarrow 2Ag + 2NO_2 + O_2$$

The residue is dissolved in dil.  $H_2SO_4$  to obtain  $CuSO_4$ .  $CuSO_4$  is treated with iron scrap to get Cu.

$$Fe + CuSO_4 \longrightarrow Cu + FeSO_4$$

## 6.37.3 SILVER OXIDE [Ag<sub>2</sub>O]

**Preparation:** It is prepared as brown solid by adding sodium hydroxide solution to silver nitrate solution.

$$2AgNO_3 + 2NaOH \longrightarrow [2AgOH] \longrightarrow Ag_2O\downarrow + H_2O$$

**Properties:** 

- 1. It is brown solid and sparingly soluble in water.
- 2. On heating, it is decomposed to black metallic silver with evolution of oxygen at 160°C

$$2Ag_2O \xrightarrow{\Delta} 4Ag + O_2\uparrow$$

**3.** The aqueous solution is strongly basic, solution behaving as AgOH. Moist silver oxide hydrolyses the alkyl halide to alcohol.

$$C_2H_5Br + AgOH \longrightarrow C_2H_5OH + AgBr$$

**4.** Dry distillation of a mixture of alkyl halide with silver oxide produces ether.

$$2C_2H_5Br + Ag_2O \xrightarrow{\Delta} C_2H_5 - O - C_2H_5 + 2AgBr$$

5. It forms colourless soluble complexes with ammonia. KCN and sodium thiosulphate.

$$Ag^{\oplus} + 2NH_4OH \longrightarrow [Ag(NH_3)_2]OH + H_2O + H^{\oplus}$$
  
Diamnine silver(1) hydroxide (Tollens reagent)

$$2Ag^{\oplus} + 4KCN \longrightarrow 2K[Ag(CN)_2] + 2K^{\oplus}$$

Potassium dicyano argenate(1)

$$\begin{array}{c} Ag^{\oplus} + 2Na_2S_2O_3 & \longrightarrow Na_3[Ag(S_2O_3)_2] + Na^{\oplus} \\ & \text{Sodium bis-thiosulphatoargenate( I)} \end{array}$$

6. It is reduced to the metal by hydrogen on heating  $Ag_2O + H_2 \xrightarrow{\Delta} 2Ag + H_2O$ 

Uses:

- 1. It is used as Tollen's reagent for the detection of aldehydes, formic acid and terminal alkynes.
- 2. It is used in the manufacture of mirrors.

# 6.37.4 SILVER THIOSULPHATE [Ag<sub>2</sub>S<sub>2</sub>O<sub>3</sub>]

#### Preparation:

- 1. When sodium thiosulphate, Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> is added to a solution of silver acetate or nitrate or fluoride, a white precipitate of silver thiosulphate is formed.
  - (i)  $2AgF + Na_2S_2O_3 \longrightarrow 2NaF + Ag_2S_2O_3 \downarrow$
  - (ii)  $S_2O_3^{2-} + Ag^{\oplus} \longrightarrow [Ag(S_2O_3)_2]^{3-}$  $\begin{array}{ccc} Ag_2S & \xrightarrow{with} & Ag_2S_2O_3\\ \text{black ppt.} & & \text{white ppt.} \end{array}$  $Ag_2S + H_2SO_4$

#### Properties:

1. It forms needle like crystals. It dissolves in excess of sodium thiosulphate solution producing a complex.

$$Ag_2S_2O_3 + 3Na_2S_2O_3 \longrightarrow 2Na_3[Ag(S_2O_3)_2]$$

2. Silver thiosulphate is decomposed by water giving a variety of colours, changing from white to black through yellow and

$$Ag_2S_2O_3 + H_2O \longrightarrow H_2SO_4 + Ag_2S \downarrow$$

# 6.38 COMPOUNDS OF MERCURY

## 6.38.1 MERCUROUS CHLORIDE [Hg,Cl,] (CALOMEL)

#### Preparation:

- 1. It is prepared by subliming mercury and mercuric chloride.  $HgCl_2 + Hg \longrightarrow Hg_2Cl_2$
- 2. It is also prepared by mixture of mercuric sulphate, common salt and mercury.

$$HgSO_4 + 2NaCl + Hg \longrightarrow Hg_2Cl_2 + Na_2SO_4$$

#### **Properties:**

- 1. It is known as calomel and used in calomel electrode which is widely employed in connection with electrochemical measurements.
- 2. It is an ionic compound and ionises in solution to give 3

$$Hg_2Cl_2 \longrightarrow Hg_2^{2+} + 2Cl^{\odot}$$
3 ions

- 3. It is called corrosive sublimate because it is highly poisonous (corrosive) and undergoes sublimation.
- 4. It is a white powder which turns black with NH<sub>2</sub>. The reaction is used in detection of mercurous ions.

$$Hg_2Cl_2 + 2NH_3 \longrightarrow (Hg + HgNH_2Cl) + NH_4Cl$$
  
Brownish-black

5. It is non-poisonous.

# 6.38.2 MERCURIC CHLORIDE [HgCl<sub>2</sub>] (CORROSIVE SUBLIMATE)

## Preparation:

1. Mercuric chloride is formed by the action of chlorine on Hg.

$$Hg + Cl_2 \longrightarrow HgCl_2$$

2. It is also formed by a mixture of mercuric sulphate and common salt.

$$HgSO_4 + 2NaCl \longrightarrow HgCl_2 + Na_2SO_4$$

## **Properties:**

- 1. It is a colourless crystalline solid, soluble in hot water
- 2. It is a covalent compound and does not ionise in the solution It is a poisonous compound and its antidote is white of  $a_0$ egg.
- 3. Its characteristic reactions are with SnCl<sub>2</sub>, NH<sub>3</sub> and KI

i. 
$$2\text{HgCl}_2 + \text{SnCl}_2 \longrightarrow \text{Hg}_2\text{Cl}_2 + \text{SnCl}_4$$
  
 $\text{Hg}_2\text{Cl}_2 + \text{SnCl}_2 \longrightarrow 2\text{Hg} + \text{SnCl}_4$ 

ii. 
$$HgCl_2 + 2NH_3 \longrightarrow HgNH_2Cl + NH_4Cl$$

iii. 
$$HgCl_2 + 2KI \longrightarrow HgI_2 + 2KCl$$
  
 $HgI_2 + 2KI \longrightarrow K_2HgI_4$ 

(A solution of this complex in alkali in called Nessler's reagent.)

4. Its very dilute solution (0.1%) is used as an antiseptic.

## 6.38.3 MERCURIC IODIDE [Hgl,]

1. It is prepared by reacting HgCl, with KI.

$$HgCl_2 + 2KI \longrightarrow HgI_2 + 2KCl$$

2. It is a yellow solid below 400 K but changes to red soild above 400 K.

$$HgI_2 \stackrel{400 \text{ K}}{=} HgI_2$$
Red Yellow

3. It dissolves in excess of KI forming K<sub>2</sub>HgI<sub>4</sub>.

$$HgI_2 + 2KI \longrightarrow K_2[HgI_4]$$

4. Alkaline solution of K<sub>2</sub>[HgI<sub>4</sub>] is called Nessler's reagent Thermal decomposition of  $Hg(NO_3)_2$ :

$$Hg(NO_3)_2 \xrightarrow{\Delta} Hg + 2NO_2 + O_2$$

## ILLUSTRATION 6.24

Write balanced equations for the reaction of alkaline perbromate with zinc giving tetrahydraoxozincate anion.

**Sol.** 
$$\operatorname{BrO_4}^{\ominus} + \operatorname{Zn} + 2\operatorname{OH}^{\ominus} + \operatorname{H_2O} \longrightarrow \operatorname{BrO_3}^{\ominus} + \operatorname{Zn}(\operatorname{OH})_4^{2^-}$$

#### ILLUSTRATION 6.25

Excess of dilute sodium hydroxide solution is gradually added with shaking to an aqueous solution of zinc sulphate. What would you observe?

Sol. 
$$ZnSO_4 + 2NaOH \longrightarrow Na_2SO_4 + Zn(OH)_2(White)$$
  
 $\xrightarrow{NaOH} Na_2ZnO_2(Soluble and colourless)$ 

# LUSTRATION 6.26

Explain the following:

The addition of NaOH solution to a solution of zinc chloride produces a white precipitate which dissolves on further addition of NaOH.

The addition of NH<sub>4</sub>OH to ZnSO<sub>4</sub> solution produces white precipitate but no precipitate is formed if it contains NH<sub>4</sub>Cl.

First a white precipitate of Zn(OH)<sub>2</sub> is formed which on further addition of NaOH forms soluble zincate Na<sub>2</sub>ZnO<sub>2</sub>. <sub>b. NH4</sub>OH is a weak hydroxide. It is ionised slightly furnishing OH<sup>©</sup> ions which are sufficient to precipitate Zn(OH)<sub>2</sub> because its low solubility product. However, in presence of NH<sub>4</sub>Cl, the ionisation of NH<sub>4</sub>OH is further suppressed and sufficient  $OH^{\Theta}$  are not available to cause precipitation.

# ILLUSTRATION 6.27

Mercurous chloride turns black on adding NH4OH to it. Explain.

$$Hg_2Cl_2 + NH_4OH \longrightarrow Hg - NH_2Cl + Hg$$
Black

This is used to detect mercurous ions.

## ILLUSTRATION 6.28

Identify A, B, C, D and E.

A white substance A reacts with dilute H2SO4 to produce a colourless gas B and a colourless solution C. The reaction between B and acidified K2Cr2O7 solution produces a green solution and a slightly coloured precipitate D. The substance D burns in air to produce a gas E which reacts with B to yield Dand a colourless liquid. Anhydrous copper sulphate is turned blue on addition of this colourless liquid. Addition of aqueous NH<sub>3</sub> or NaOH to C produces first a precipitate, which dissolves in the excess of the respective reagent to produce a clear solution in each case.

$$\begin{array}{l} \text{Sol.} \ ZnS(A) + dil. \ H_2SO_4 \longrightarrow H_2S(B) + ZnSO_4(C) \\ 3H_2S + Cr_2O_7^{2-} + 8H^{\oplus} \longrightarrow 2Cr^{3+}(Green) + 3S(D) + 7H_2O \\ S(D) + O_2 \longrightarrow SO_2(E) \\ SO_2(E) + H_2S(B) \longrightarrow S(D) + H_2O(Colourless \ liquid) \\ Zn^{2+} + 2OH^{\ominus} \longrightarrow 2n(OH)_2 \downarrow \stackrel{OH^{\ominus}}{\longrightarrow} Zn(OH)_4^{2-} \\ & (Clear \ solution) \ (C) \end{array}$$

# CONCEPT APPLICATION EXERCISE 6.2

# Compounds of Fe:

1. Complete and balance the following equations:

i. 
$$FeSO_4 \xrightarrow{1. K_2Cr_2O_7} \underbrace{1. K_2Cr_2O_7}_{2. K_4[Fe(CN)_6]}$$
ii.  $FeSO_4 \xrightarrow{\text{to redness}}$ 

- 2. Explain the following:
  - i. FeCl<sub>3</sub> and FeBr<sub>3</sub> are well known, but FeI<sub>3</sub> has doubtful existence.
  - ii. Anhydrous FeCl<sub>3</sub> cannot be obtained by heating hydrated ferric chloride.
  - iii. Cast iron is hard but pure iron is soft in nature.
  - iv A ferrous salt decolourises KMnO<sub>4</sub> solution.
  - v. A ferrous salt turns brown in air.
- 3. Draw shape of FeCl<sub>2</sub> in:
  - i. Water
  - ii. Ether
  - iii. Gaseous state
- **4.** What happen when iron is treated with:
  - i. Steam
  - ii. Dilute HNO<sub>3</sub>
- 5. Colourless salt A decolourises I<sub>2</sub> solution and gives white precipitate with AgNO3 solution. A also changes FeCl3 (yellow solution of FeCl<sub>2</sub> (Green). Identify A and explain the reactions.
- 6. Iron forms iron(II) chloride, FeCl, and iron(III) chloride FeCl<sub>3</sub>. One of these chlorides is a dark brown solid melting 306°C. The other is a white crystalline solid with greenish tint, melts at 674°C. Which description best fits iron(II) chloride. Explain.
- 7. Account for the following observations and write balanced chemical equations for them.
  - i. When ferrous sulphate crystals are exposed to air, it turns brown.
  - ii. A solution of ferric chloride in water gives a brown precipitate on standing.

#### Compounds of Cu:

- 8. When copper is exposed to atmosphere for a longer time, a green mass deposits on its surface. Discuss the chemical reaction involved.
- Complete and balance the following equations:  $CuS + 2H_2SO_4 + \dots \longrightarrow 2CuSO_4 + 2H_2O + S$
- 10. Explain the following:
  - i. Copper hydroxide is soluble in ammonium hydroxide but not in sodium hydroxide.
  - ii. A dark blue precipitate is formed when sodium hydroxide solution is added to copper sulphate solution. The precipitate darkens on heating.

## Compounds of Zn:

- i. ZnO is used as a white paint inspite of the fact that it has less covering power than white lead.
  - ii. Hydrated ZnCl<sub>2</sub> cannot be dehydrated on heating?
  - iii. Zn is used in galvanisation of Fe.

## Compounds of Ag:

- 12. Preparation of looking mirrors involves the use of ammonical AgNO3, red lead and HCHO. Explain the function of each.
- 13. Give reasons for the following:
  - i. Silver ornament gets tarnished when exposed to atmosphere for a long time.

ii. Silver nitrate solution is kept in dark coloured bottles.

iii. Why does AgNO<sub>3</sub> produce a black stain on the skin.

## Compounds of Hg:

- 14. An aqueous solution containing one mole of HgI, and two moles of NaI is orange in colour. On addition of excess NaI the solution becomes colourless. The orange colour reappears on subsequent addition of NaOCl. Explain with equations.
- 15. HgCl<sub>2</sub> and SnCl<sub>2</sub> cannot coexist together in an aqueous solution.
- 16. Complete and balance the following equations:

i. 
$$Cu(OH)_2 + NH_4NO_3 + NH_4OH \longrightarrow ... + H_2O$$

ii. 
$$Au + HCl + HNO_3 \longrightarrow ... + ... + H_2O$$

iii. 
$$Ag_2S + 2CuCl_2 + 2Hg \longrightarrow ... + ... S + 2Ag$$

iv. 
$$FeCl_3 + KI \longrightarrow ....$$

v. 
$$Fe^{2+} + NO_3^{\ominus} + H^{\oplus} \longrightarrow Fe^{3+} + ... H_2O$$

vi. 
$$MnO_4^{\Theta} + Fe^{2+} \longrightarrow Mn^{2+} + Fe^{3+} + H_2O$$

vii. 
$$FeCl_3 + H_2S \longrightarrow$$

viii. 
$$HgCl_2 + SO_2 + ... \longrightarrow ...$$

ix. 
$$CdSO_4 + NH_4OH \longrightarrow ...$$

$$\mathbf{x}$$
.  $\mathrm{HgCl}_2 + \mathrm{SnCl}_2 \longrightarrow ...$ 

**xi.** 
$$Ag + CN^{\Theta} + O_2 + ... \longrightarrow ... OH^{\Theta} + ...$$

xii. 
$$CuSO_4 + KCN \longrightarrow ...$$

xiii. 
$$CuSO_4 + KI \longrightarrow ...$$

**xiv.** 
$$CuSO_4 + NH_4OH \longrightarrow ... + ...$$

## Solved Examples

#### EXAMPLE 6.1

Explain why mercury (I) ion exists as Hg<sub>2</sub><sup>2+</sup> ion while copper (I) ion exists as Cu<sup>⊕</sup> ion.

**Sol.** 
$$Hg(Z = 80) \Rightarrow 4f^{14} 5d^{10} 6s^2; Hg^{\oplus} \Rightarrow 4f^{14} 5d^{10} 6s^1$$

Hg<sup>⊕</sup> has one electron in its valence 6s-orbital, due to this Hg<sup>⊕</sup> compounds should be paramagnetic but actually they are diamagnetic. Hence the singly filled 6s-orbitals of the two Hg<sup>®</sup> ions overlap to form a Hg-Hg covalent bond. Thus, Hg<sup>®</sup> ions exist as dimeric species, i.e. Hg<sub>2</sub><sup>2+</sup>

$$Cu(Z=29) \implies 3d^{10} 4s^{1}$$

$$Cu^{\oplus} \Rightarrow 3d^{10}$$

Therefore, Cu<sup>®</sup> ion has no unpaired electrons to form dimeric species, i.e. Cu<sub>2</sub><sup>2+</sup> and hence it always exists as Cu<sup>®</sup> ion.

#### EXAMPLE 6.2

Give reasons for the following:

Variations in the radii of transition elements are not as pronounced as those of representative elements.

Sol. As we proceed along a transition series, the nuclear charge increases which tends to decrease the size but the addition of increases which terms in the d-subshell increases the screening effect  $w_{hich}$  electrons in the d-subshell increased the increased  $w_{hich}$ tends to counterbalance the effect of the increased nuclear charge

## EXAMPLE 6.3

Why in any transition series, melting points first increase and then decrease and also they show a dip in the middle?

Sol. Melting points first increase because the number of unpaired electrons increases and hence strength of metallic bond increases. After reaching the maximum, the melting points decrease because the pairing of electron starts in the d-subshell and number of unpaired electrons decreases and so the strength of metallic bond decreases. The dip in the middle is due to exactly half-field configuration of d-subshell which has higher stability Hence electrons are held tightly by the nucleus. As a result, metallic bond is weaker.

## EXAMPLE 6.4

Atomic radius of Cu is greater than that of Cr but ionic radius of Cr<sup>2+</sup> is greater than that of Cu<sup>2+</sup>. Give suitable explanation

**Sol.** In Cu, all the *d*-electrons are paired  $(3d^{10}4s^1)$ . In Cr, all the d-electrons are unpaired  $(3d^54s^1)$ . Hence, d-d electron repulsions in Cu are much greater than those in Cr. Hence, Cu atom is larger in size than Cr. In  $Cu^{2+}(3d^9)$ , d-d electron repulsions decrease due to presence of one unpaired d-electron. Moreover, the electrons are attracted. by 29 protons of the nucleus whereas in Cr<sup>2-</sup>, three unpaired electrons are still present but they are attracted by only 24 protons of the nucleus. Thus, Cu<sup>2+</sup> is smaller in size than Cr<sup>2</sup>

#### EXAMPLE 6.5

Why hydrated copper sulphate is blue while anhydrous copper sulphate is white?

Sol. In CuSO<sub>4</sub>·5H<sub>2</sub>O four water, molecules are present is ligands. In the presence of these ligands d-orbitals are no longer degenerate in energy. Hence d-d transition takes place absorbing red wavelength. The complementary colour, viz., blue is reflected In anhydrous  $\text{CuSO}_4$ , d-orbitals remain degenerate. Hence, no d-dtransition can occur. The white light is completely reflected back Hence, it looks white.

#### EXAMPLE 6.6

Why are the ionisation energies of 5d elements greater than 3d elements?

**Sol.** In the 5d series, after lanthanium (Z = 57), there is lanthanoid contraction. In each group, the size of 5d element is smaller while nuclear charge is greater than 3d element. Hence, ionisation energies of 5d elements are greater than 3d elements.

## EXAMPLE 6.7

Explain why cuprous chloride (CuCI) is colourless white cupric chloride (CuCl<sub>2</sub>) is blue? or TiCl<sub>3</sub> is coloured while TiCl<sub>4</sub> <sup>[5]</sup> colourless?

In CuCl, Cu<sup> $\oplus$ </sup> has fully-filled *d*-subshell. Hence, it cannot energy for *d*–*d* transition. Therefore, it is colourless. In  $^{abs0rb}$  cu<sup>2+</sup> has  $3d^9$  configuration, i.e., one unpaired electron is  $^{CuCl}$ 2. which can absorb energy for *d*–*d* transition. Hence, it is  $^{absorb}$ 3.

 $\frac{coloureu.}{similarly}$ ,  $Ti^{3+}$  has  $3d^1$  and  $Ti^{4+}$  has empty 3d subshell. Hence,  $\frac{coloured}{cl_3}$  is coloured while  $TiCl_4$  is colourless.

# EXAMPLE 6.8

The sums of first and second ionisation energies and those of third and fourth ionisation energies of nickel and platinum are:

$IE_3 + IE_4 (MJ \text{ mol}^{-1})$
8.80
6.70

Based on this information, write

- i. The most common oxidation states of Ni and Pt and why.
- ii. Name of the metal (Ni or Pt) which can more easily form compounds in its +4 oxidation state and why.

#### Sal.

- i. The sum of the 3rd and 4th ionisation energies of nickel is much higher than the sum of 1st and 2nd ionisation energies. Hence, Ni (II) is more common. In case of platinum, the difference between IE<sub>3</sub> + IE<sub>4</sub> and IE<sub>1</sub> + IE<sub>2</sub> is much less. Hence, Pt (IV) is more common.
- ii. For Ni,  $IE_1 + IE_2 + IE_3 + IE_4$ = 2.49 + 8.80 = 11.29 kJ mol<sup>-1</sup> For Pt,  $IE_1 + IE_2 + IE_3 + IE_4$ = 2.66 + 6.70 = 9.36 kJ mol<sup>-1</sup>.

Thus, the formation of Pt<sup>4+</sup> is easier than Ni<sup>4+</sup>. In other words, Pt can form compounds in the +4 oxidation state more easily.

#### EXAMPLE 6.9

Describe giving reason which one of the following pairs has the property indicated?

- a. Fe or Cu has higher melting point.
- b. Co<sup>2+</sup> or Ni<sup>2+</sup> has lower magnetic moment.

#### Sol.

- a. Fe has higher melting point than Cu. This is because Fe has four unpaired electrons in 3d-subshell while Cu has only one electron in the 4s-soubshell. Hence, metallic bonds in Fe are much stronger than those in Cu.
- b.  $Co(Z = 27) \Rightarrow 3d^74s^2$ ,  $Co^{2+} = 3d^7(3 \text{ unpaired electron})$   $Ni(Z = 28) \Rightarrow 3d^84s^2$ ,  $Ni^{2+} = 3d^8(2 \text{ unpaired electron})$ Hence, Ni has lower magnetic moment than Co.

# EXAMPLE 6.10

Give reasons for the following features of transition metal chemistry:

The lowest oxide of a transition metal (say, chromium, atomic number 24) is basic whereas the highest oxide is usually acidic.

ii. Transition metals sometimes exhibit very low oxidation states such as + 1 and 0.

#### Sol.

- Lowest oxide of Cr is CrO which is basic. The highest oxide is CrO<sub>3</sub> which is acidic. (In between, Cr<sub>2</sub>O<sub>3</sub> is amphoteric). Higher the oxidation state of the metal, more easily it can accept electrons and hence greater is the acidic character.
- ii. The +1 oxidation state is shown by Cu because after loss of one electron, it acquires stable configuration of  $3d^{10}$ . Zero oxidation state is shown in forming metal carbonyls, e.g., Ni(CO)<sub>4</sub> because  $\pi$ -electrons donated by the ligands are accepted into the empty d orbitals.

### EXAMPLE 6.11

The 4d and 5d series of transition metals have more frequent metal-metal bonding in their compounds than do the 3d metals. Explain.

Sol. In the same group of d-block elements, the 4d and 5d transition element has larger size than that of 3d element. Thus, the valence electrons are less tightly held and hence can form metal-metal bond more frequently. (That is why melting points of 4d and 5d series as well as enthalpies of atomisation are higher than those of 3d series).

#### EXAMPLE 6.12

- **a.** K<sub>2</sub>PtCl<sub>6</sub> is a well known compound whereas corresponding Ni compound is not known. State a reason for it.
- b. Most of the transition metals do not displace hydrogen from dilute acids. Why?
- c. Why have the transition elements high enthalpy of hydration?
- **d.** Chromium is a typical hard metal while mercury is a liquid. Explain why?

#### Sol.

- a. This is because Pt<sup>4+</sup> is more stable than Ni<sup>4+</sup> as the sum of four ionisation enthalpies of Pt is less than that of Ni.
- **b.** This is because most of the transition metals have negative oxidation potentials.
- c. This is due to their small size and large nuclear charge. This is so because when we move along any transition series, the nuclear charge increases and size decreases.
- **d.** Cr has five unpaired d electrons in the d-subshell  $(3d^54s^1)$ . Hence, metallic bonds are very strong. In Hg, all the d-orbitals are fully filled  $(3d^{10} 4s^2)$ . Hence, the metallic bonding is very weak.

#### EXAMPLE 6.13

- a. Of the lanthanides, cerium (Z = 58) forms a tetrapositive ion,  $Ce^{4+}$  in aqueous solution. Why?
- **b.** The +3 oxidation states of lanthanum (Z = 57), gadolinium (Z = 64) and lutetium (Z = 71) are especially stable. Why?
- c. Why Zr and or Nb and Ta exhibit similar properties?
- **d.** Which out of the two, La(OH)<sub>3</sub> and Lu(OH)<sub>3</sub>, is more basic and why?

#### Sol.

- **a.**  $Ce^{3+}$  having the configuration  $4f^{1}5d^{0}6s^{0}$  can easily lose an electron to acquire the configuration 4f 0 and form Ce4+. In fact, this is the only +4 state lanthanide which exists in
- b. This is because they have empty, half-filled and completely filled 4f sub-shell respectively.
- c. Due to the consequence of lanthanoid contraction, Hf (Z = 72) has size similar to that of Zr (Z = 40). Hence, their properties are similar. For the same reason, Nb and Ta have similar size and hence similar properties.
- d. La(OH)<sub>3</sub> is more basic than Lu(OH)<sub>3</sub>. As the size of the lanthanoid ions decreases from La<sup>3+</sup> to Lu<sup>3+</sup>, the covalent character of the hydroxides increases (Fajan's rules). Hence, the basic strength decreases from La(OH)3 to Lu(OH)3.

## EXAMPLE 6.14

- a. Why second and third transition series elements show similar
- b. Why electronic configurations of lanthanoids are not known with certainty?
- The electronic configurations of actinide elements are not known with certainty. Explain.
- d. Why there is similarities (horizontal and vertical) in successive members of the transition series?

#### Sol.

- a. In the third transition series after lanthanum, there is lanthanoid contraction. Due to this contraction, the size of any atom of the third transition series is almost the same as that of the element lying just above in the second transition series. This leads to similarity in their properties.
- **b.** In the lanthanoids, 4f and 5d subshells are very close in energy. The outermost 6s orbital remains filled with 2 electrons ( $6s^2$ ). The electron can easily jump from 4f to 5dor vice versa. Hence, their electronic configurations are not known with certainty.
- **c.** In actinides, 5f and 6d subshells are close in energy. Hence, they show a large number of oxidation states. The electrons can jump from 5f to 6d or vice versa. Hence, their electronic configuration are not known with certainty.
- d. This is because of the fact that along a horizontal row, electrons enter an incomplete inner shell in building up an atom, while the outer level remains almost unchanged. In vertical columns, similarities are due to similar electronic configurations even in the d-subshells.

#### EXAMPLE 6.15

- a. Chemistry of all the lanthanoids is quite similar.
- b. The actinide contraction differs from lanthanide contraction? Explain.
- A serious accident occurred in a chemistry laboratory when a student tried to dissolve excess of KMnO<sub>4</sub> in conc. H<sub>2</sub>SO<sub>4</sub>.

#### Sol.

- a. The change in the size of the lanthanoids due to lanthanoid The change in the same than the contraction is very small as we proceed from La (Z = 57)to Lu (Z=71). Hence, their chemical properties are similar Moreover, their valence shell configuration remains the same because the electrons are added into the inner 4f-subshell Hence, they show similar chemical properties.
- b. Lanthanide contraction refers to the gradual decrease in the size of the lanthanoids and their trivalent  $i_{0\eta_S}$ in the size of the (Z = 58 to 71) whereas actinoid series refers to the gradual decrease in the size of the actinoids or their ions (M<sup>3+</sup> or M<sup>4+</sup>) (Z = 90 to 103). They differ in the fact that in the actinoid series, the contraction is greater from element to element due to poor shielding by 5f electrons than by 4f electrons.
- c. This is due to the formation of high explosive oily substance Mn<sub>2</sub>O<sub>7</sub> which is responsible for the accident  $2KMnO_4 + H_2SO_4 \longrightarrow K_2SO_4 + Mn_2O_7 + H_2O_1$

$$2Mn_2O_7 \xrightarrow{Explodes} 4MnO_2 + 3O_2$$

#### EXAMPLE 6.16

Identify A to E. Pyrolusite on heating with KOH in the presence of air gives a dark green compound (A). The solution of (A) on treatment with H2SO4 gives a purple coloured compound (B) which gives the following reactions:

- a. KI on reaction with alkaline solution of (B) changes into a compound (C).
- b. The colour of the compound (B) disappears on treatment with the acidic solution of FeSO<sub>4</sub>.
- c. With conc. H<sub>2</sub>SO<sub>4</sub> compound (B) gives (D) which can compose to yield (E) and oxygen.

Sol. 
$$2MnO_2 + 4KOH + O_2 \longrightarrow 2K_2MnO_4 + 2H_2O$$
(Air) (A) Dark green

$$3K_2MnO_4 + 2H_2SO_4 \longrightarrow 2KMnO_4 + MnO_2 + 2K_2SO_4 + 2H_2O_4$$
(B) Purple

a. 
$$2KMnO_4 + H_2O + KI \longrightarrow KIO_3(C) + 2MnO_2 + 2KOH$$

**b.** 
$$2\text{KMnO}_4 + 8\text{H}_2\text{SO}_4 + 10\text{FeSO}_4 \longrightarrow \text{K}_2\text{SO}_4 + 2\text{MnSO}_4 + 5\text{Fe}_2(\text{SO}_4)_3 + 8\text{H}_20$$

c. 
$$2KMnO_4 + H_2SO_4 \longrightarrow Mn_2O_7(D) + K_2SO_4 + H_2O_4$$
  
 $2Mn_2O_7 \longrightarrow 4MnO_2(E) + 3O_2$ 

#### EXAMPLE 6.17

Identify A to F.

a. 
$$\text{CuSO}_4 \cdot 5\text{H}_2\text{O} \xrightarrow{100^{\circ}\text{C}} (\text{A}) \xrightarrow{230^{\circ}\text{C}} (\text{B}) \xrightarrow{720^{\circ}\text{C}} (\text{C})^{+} (\text{D})$$

**b.** AgNO<sub>3</sub> 
$$\xrightarrow{\text{Red hot}}$$
 (E) + (F) + O<sub>2</sub>

a. (A) 
$$CuSO_4.5H_2O \xrightarrow{100^{\circ}C} CuSO_4.4H_2O \xrightarrow{230^{\circ}C}$$

Blue

Bluish white

$$CuSO_{4} \xrightarrow{720^{\circ}C} CuO + SO_{2} + \frac{1}{2}O_{2} \xrightarrow{1100^{\circ}C} Cu_{2}O + O_{2}$$
White Black Red

# $(E)^{Ag}$ ; $(F)^{NO_2}$ ; $2Ag^{NO_3} \longrightarrow 2Ag + 2NO_2 + O_2$

# EXAMPLE 6.18

Identify A to E.

Apowdered substance (A) on treatment with fusion mixture Apriles a green coloured compound (B).

The solution of (B) in boiling water on acidification with dilute H<sub>2</sub>SO<sub>4</sub> gives a pink coloured compound (C).

The aqueous solution of (A) on treatment with NaOH and Br,-water gives a compound (D).

A solution of (D) in conc. HNO<sub>3</sub> on treatment with lead peroxide at boiling temperature produced a compound (E) which was of the same colour as that of (C).

A solution of (A) in dilute HC1 on treatment with a solution of barium chloride gave a white precipitate of compound (F) which was insoluble in conc. HNO<sub>3</sub> and conc. HCl.

$$\underset{\text{(A)}}{\text{MnSO}_4} + \text{Na}_2\text{CO}_3 + 2\text{KNO}_3 \longrightarrow \text{Na}_2\text{MnO}_4 + 2\text{KNO}_2$$
(B) Green coloured

<sub>b.</sub> 
$$3Na_2MnO_4 + 2H_2SO_4 \longrightarrow 2NaMnO_4 + MnO_2 +$$
(C) Pink coloured

$$2Na_2SO_4 + 2H_2O$$

c. 
$$MnSO_4 + 4NaOH + Br_2 \longrightarrow MnO_2 + Na_2SO_4 + 2NaBr$$

(D) 
$$+ 2H_2O$$

d. 
$$2MnO_2 + 10HNO_3 + 5PbO_2 \longrightarrow 2HMnO_4 + 5Pb(NO_3)_2$$
(E) Pink coloured

$$+4H_{2}O + O_{2}$$

e. 
$$MnSO_4 + BaCl_2 \longrightarrow BaSO_4 + MnCl_2$$
(F) (Insoluble in conc.  $HNO_3$  and conc.  $HCl$ )

## EXAMPLE 6.19

Identify A to G.

<sup>1</sup> An ore (A) on roasting with sodium carbonate and lime in the presence of air gives two compounds, (B) and (C).

h. The solution of (B) in conc. HCl on treatment with potassium ferrocyanide gives a blue colour or precipitate of compound (D).

<sup>t.</sup> The aqueous solution of (C) on treatment with conc. H<sub>2</sub>SO<sub>4</sub> gives a yellow coloured compound (E).

4. Compound (E) when treated with KCI gives an orange-red compound (F) which is used as an oxidising reagent.

Fine solution of (F) on treatment with oxalic acid and then with an excess of potassium oxalate gives blue crystals of compound (G).

<sup>a, 4</sup>FeO·Cr<sub>2</sub>O<sub>3</sub>(A) + 
$$8$$
Na<sub>2</sub>CO<sub>3</sub> +  $7$ O<sub>2</sub>  $\longrightarrow$  Lime

$$2Fe_2O_3(B) + 8Na_2CrO_4(C) + 8CO_2$$

$$\begin{array}{c}
\text{2Fe}_2\text{O}_3(\text{B}) + 8\text{N} \\
\text{Fe}_2\text{O}_3(\text{B}) + 6\text{HCl} \longrightarrow 2\text{FeCl}_3 + 3\text{H}_2\text{O} \\
\text{4FeCl}_3 + 3\text{K} \text{ Fe}_2(\text{CD}) & \text{Fe}_2(\text{CD})
\end{array}$$

$${}^{4FeCl_{3}+3K_{4}Fe(CN)_{6}} \longrightarrow Fe_{4}[Fe(CN)_{6}]_{3}(D) + 12KCl$$
Prussian blue

c.  $2\text{Na}_2\text{CrO}_4(C) + \text{H}_2\text{SO}_4 \longrightarrow \text{Na}_2\text{Cr}_2\text{O}_7(E) + \text{Na}_2\text{SO}_4 + \text{H}_2\text{O}$ Yellow coloured

**d.** 
$$Na_2Cr_2O_7 + 2KCl \longrightarrow K_2Cr_2O_7(F) + 2NaCl$$
Orange-red

e. 
$$K_2Cr_2O_7 + 4H_2SO_4 + 3H_2C_2O_4 \longrightarrow K_2SO_4 +$$

$$Cr_2(SO_4)_3 + 6CO_2 + 7H_2O$$

$$Cr_2(SO_4)_3 + 6K_2C_2O_4 \longrightarrow 2K_3[Cr_2(C_2O_4)_3](G) + 3K_2SO_4$$
Blue crystals

## EXAMPLE 6.20

Identify A to C.

- a. An aqueous solution of a compound (A) is acidic towards litmus and (A) is sublimed at about 300°C.
- b. (A) on treatment with an excess of NH<sub>4</sub>CNS gives a red coloured compound (B) and on treatment with a solution of K<sub>4</sub>Fe(CN)<sub>6</sub> gives a blue coloured compound (C).

Sol. (A) is FeCl<sub>3</sub>. It gives red colour of Fe(CNS)<sub>3</sub> with NH<sub>4</sub>CNS and chromyl chloride test for Cl<sup>©</sup> ion. The reactions are:

**b.** 
$$FeCl_3 + 3NH_4CNS \longrightarrow Fe(CNS)_3 + 3NH_4Cl$$
(B) Red
$$4FeCl_3 + 3K_4Fe(CN)_6 \longrightarrow Fe_4[Fe(CN)_6]_3 + 12KCl$$
(C) Blue

#### EXAMPLE 6.21

Identify A.

- a. Compound (A) on strong heating gives two oxides of sulphur.
- b. On adding aqueous NaOH solution to its aqueous solution, a dirty green precipitate is obtained which starts brown on exposure to air.

Sol. 
$$2\text{FeSO}_4 \xrightarrow{\text{Heat}} \text{Fe}_2\text{O}_3 + \text{SO}_2 + \text{SO}_3$$
(A)

FeSO<sub>4</sub> + 2NaOH  $\longrightarrow$  Fe(OH)<sub>2</sub> + Na<sub>2</sub>SO<sub>4</sub>

Fe(OH)<sub>2</sub>  $\xrightarrow{[O]}$  Fe(OH)<sub>3</sub>

#### EXAMPLE 6.22

How the following conversions are made? Explain only by giving chemical equations.

- Copper chloride from copper nitrate.
- Cuprous oxide from copper sulphate.
- Cuprous oxide from copper.
- Mercuric chloride from mercuric sulphate.
- Anhydrous ZnCl<sub>2</sub> from white vitriol. e.
- Zinc carbonate from zinc oxide.
- Ferrous sulphate from ferrous ammonium sulphate.
- **h.** Prussian blue from  $K_4$ Fe(CN)<sub>6</sub>.
- Lithopone from white vitriol. i.
- Cuprous iodide from copper sulphate. j.

Sol.

**a.** 
$$Cu(NO_3)_2 + 2NaOH \longrightarrow Cu(OH)_2 + 2NaNO_3$$
ppt.

$$Cu(OH)_2 + 2HCl \longrightarrow CuCl_2 + 2H_2O$$

**b.** 
$$\text{CuSO}_4 + 2\text{NaOH} \longrightarrow \text{Cu(OH)}_2 + \text{Na}_2\text{SO}_4$$

$$Cu(OH)_2 \xrightarrow{Strongly} CuO + H_2O$$

$$CuO + Cu \xrightarrow{\text{Heat}} Cu_2O$$
Powder

or 
$$CuSO_4 \longrightarrow Fehling's solution$$

$$C_6H_{12}O_6$$
 + Fehling's soln.  $\longrightarrow Cu_2O + C_6H_{12}O_7$ 
Glucose Red ppt. Gluconic acid

c. 
$$Cu + 4HNO_3 (conc.) \longrightarrow Cu(NO_3)_2 + 2NO_2 + 2H_2O$$
  
 $2Cu(NO_3)_2 \xrightarrow{Heat} 2CuO + 4NO_2 + O_2$ 

$$CuO + Cu \xrightarrow{Heat} Cu_2O$$

d. By heating a solid mixture of HgSO<sub>4</sub> and NaCl.

$$HgSO_4 + 2NaCl \xrightarrow{Heat} HgCl_2 + Na_2SO_4$$

e. 
$$ZnSO_4 \cdot 7H_2O \xrightarrow{Strongly} ZnSO_4 + 7H_2O$$

White vitriol

$$ZnSO_4 \xrightarrow{Heat} ZnO + SO_3$$
  
 $ZnO + 2HC1 \longrightarrow ZnCl_2 + H_2O$ 

$$ZnCl_2 + 2NH_4Cl \longrightarrow ZnCl_2 \cdot 2NH_4Cl$$

Double salt

$$ZnCl_2 \cdot 2NH_4Cl \xrightarrow{Heat} ZnCl_2 + 2NH_4Cl$$

Anhydrous

f. 
$$ZnO + H_2SO_4 \longrightarrow ZnSO_4 + H_2O$$

$$ZnSO_4 + 2NaHCO_3 \longrightarrow ZnCO_3 + Na_2SO_4 + H_2O + CO_2$$

g. 
$$FeSO_4(NH_4)_2SO_4 \cdot 6H_2O + 4NaOH \longrightarrow$$

$$Fe(OH)_2 + 2NH_3 + 2Na_2SO_4 + 8H_2O_{ppt}$$

$$Fe(OH)_2 + H_2SO_4 \longrightarrow FeSO_4 + 2H_2O$$

solution is put to crystallisation when crystals of ferrous sulphate,  $FeSO_4 \cdot 7H_2O$ , are obtained.

**h.** 
$$4\text{FeCl}_3 + 3\text{K}_4\text{Fe(CN)}_6 \longrightarrow \text{Fe}_4[\text{Fe(CN)}_6]_3 + 12\text{KCl}$$

Prussian blue

i. 
$$ZnSO_4 + BaS \longrightarrow ZnS + BaSO_4$$
  
Lithopone

j. 
$$2\text{CuSO}_4 + 4\text{KI} \longrightarrow \text{Cu}_2\text{I}_2 + 2\text{K}_2\text{SO}_4 + \text{I}_2$$
  
White ppt.

## EXAMPLE 6.23

Ferrochrome Fused with 
$$Na_2CO_3$$
 in excess of  $air + H_2O$  Yellow

$$(C) + Na2SO4 + H2O \xrightarrow{\Delta} (D) + 2NaCl \xrightarrow{H2O2/H\oplus} (E)$$
Orange
red
$$(E) + Na2SO4 + H2O \xrightarrow{KCl} Orange (ice cooled) Deep (ic$$

**Sol.** It is the preparation of K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>

i. 
$$4\text{FeO.Cr}_2\text{O}_3 + 8\text{Na}_2\text{CO}_3 + 7\text{O}_2 \longrightarrow 8\text{Na}_2\text{CrO}_4$$

Ferrochrome (A) (B)

ii. 
$$2\text{Na}_2\text{CrO}_4 + \text{H}_2\text{SO}_4 \longrightarrow \text{Na}_2\text{Cr}_2\text{O}_7 + \text{Na}_2\text{SO}_4 + \text{H}_2\text{O}_4$$
(B)
(C)

iii. 
$$2\text{Na}_2\text{Cr}_2\text{O}_7 + 2\text{KCl} \longrightarrow \text{K}_2\text{Cr}_2\text{O}_7 + 2\text{NaCl}$$

iv. 
$$Cr_2O_7^{2-} + 4H_2O_2 + 2H^{\oplus} \longrightarrow 2CrO_5 + 5H_2O$$
(D) (E)

## EXAMPLE 6.24

Identify A to F:

Pyrolusite 
$$\xrightarrow[\text{fred}]{\text{with}}$$
  $\xrightarrow[\text{Fused}]{\text{with}}$   $(B)$   $\xrightarrow[\text{Furple}]{\text{H}}$   $(C)$   $+$   $(A)$   $(C)$   $+$   $(A)$   $(C)$   $+$   $(C)$   $+$   $(A)$   $(C)$   $+$   $(A)$   $(C)$   $+$   $(A)$   $(C)$   $+$   $(B)$   $(C)$   $+$   $(C)$ 

$$E (gas) \xrightarrow{NH_3} F (an explosive compound)$$

Sol. It is the preparation of KMnO<sub>4</sub>.

i. 
$$2\text{MnO}_2 + 4\text{KOH} + \text{O}_2 \text{ (from KNO}_3) \longrightarrow 2\text{K}_2\text{MnO}_4 + 2\text{H}_2\text{O}_3$$
(B)

ii. 
$$3\text{MnO}_4^{2-} + 4\text{H}^{\oplus} \xrightarrow{\text{Disproportionation}} 2\text{MnO}_4^{\ominus} + \text{MnO}_2^{-+2\text{H}_2\text{O}}$$
(B)
(C)
(A)

iii. 
$$2\text{MnO}_4^{\ominus} + \text{H}_2\text{O} + \text{I}^{\ominus} \longrightarrow 2\text{MnO}_2 + \text{IO}_3^{\ominus} + 2\text{OH}^{\ominus}$$
(C) (A) (D)

iv. 
$$MnO_2 + 4Cl^{\odot} \longrightarrow MnCl_2 + Cl_2(g) + 2H_2O$$
(A) (E)

v. 
$$NH_3 + 3Cl_2$$
 (excess)  $\longrightarrow NCl_3 + 3HCl_3$ 

# **Exercises**

# Single Correct Answer Type

# Properties and Electronic Configuration

- in general, the melting and boiling points of transition
- (1) Increases gradually across the period from left to right
- (2) Decreases gradually across the period from left to right
- (3) First increases till the middle of the period and then decreases towards the end
- (4) First decreases regularly till the middle of the period and then increases towards the end
- , Which metal has the highest melting point?
- (1) Pt

(2) W

(3) Pd

- (4) Au
- 3. Which metal has the lowest melting point?
  - (1) Cs

(2) Na

(3) Hg

- (4) Sn
- The inner transition elements are the element which the added electrons go to
  - (1)(n-1) d-orbitals
  - (2) (n-2) f-orbitals
  - (3) (n-1) *d*-orbitals and (n-1) *f*-orbitals
  - (4) (n-1) d-orbitals and ns orbitals.
- 5. The electronic configuration of actinides cannot be assigned with degree of certainty because of
  - (1) Small energy difference between 5f and 6d levels
  - (2) Overlapping of inner orbitals
  - (3) Free movement of electrons over all the orbitals
  - (4) None of above
- Among the following series of transition metal ions, the one where all metal ions have  $3d^2$  electronic configuration is
- ${}^{(1)}T_1^{r^{3+}}\!,V^{2+}\!,Cr^{3+}\!,Mn^{4+}$
- (2)  $Ti^{\oplus}$ ,  $V^{4+}$ ,  $Cr^{6+}$ ,  $Mn^{7+}$
- (3)  $Ti^{4+}$ ,  $V^{3+}$ ,  $Cr^{2+}$ ,  $Mn^{3+}$
- (4)  $Ti^{2+}$ ,  $V^{3+}$ ,  $Cr^{4+}$ ,  $Mn^{5+}$
- 7. The first ionisation energies of the elements of the first transition series  $(Ti \rightarrow Cu)$ 
  - (1) Increases as the atomic number increases
- (2) Decreases as the atomic number increases
- (3) Do not show any change as the addition of electrons takes place in the inner (n-i) d-orbitals
- (4) Increases from Ti to Mn and then decreases from Mn to Cu
- 8. Which has the largest radius?
- $(1) Co^{3+}$

(2)  $Mn^{3+}$ 

 $(3) \text{ Fe}^{3+}$ 

- (4)  $Cr^{3+}$
- The atomic number of V, Cr, Mn and Fe are respectively 23, 24, 25 and 26. Which one of these may be expected to have the highest second ionisation enthalpy?

(2) Cr

 $^{(3)}Mn$ 

(4) Fe

- 10. The first ionisation energies of the elements of the transition series
  - (1) Increase as the atomic number increases
  - (2) Decrease as the atomic number increases
  - (3) Do not show any change as the addition of electron takes place in the inner (n-1) *d*-orbitals
  - (4) None of the above
- 11. Among 3d transition series the IE
  - (1) Increases regularly in moving from left to right
  - (2) Decreases regularly in moving from left to right
  - (3) Remains constant within the period
  - (4) Increases gradually within the period but the relative increase is not sharp
- 12. Which of the following is the most suitable description of transition elements?
  - (1) Low melting points
  - (2) No catalytic activity
  - (3) Show variable oxidation states
  - (4) Exhibit inert pair effect
- 13. Select the incorrect statement:
  - (1) The melting point of Mn is lower than that of Cr and Fe in 3d series.
  - (2) The melting point of Tc is higher than that of Mo but lower than that of Ru in 4d series.
  - (3) The melting point of W (tungsten) is highest in 5d series.
  - (4) The order of melting points of 3d, 4d and 5d series is: 5d > 4d > 3d
- **14.** Select the **incorrect** statement:
  - (1) The atomic radii of 4d series are larger than those of 3d series
  - (2) The atomic radii of 4d and 5d series are almost same.
  - (3) Stability of the M<sup>3+</sup> ions in aqueous solution is:  $Sc^{3+} > Cr^{3+} > Fe^{3+} > Co^{3+}$
  - (4) Basic strength of the hydroxides is:  $La(OH)_3 \le Y(OH)_3 \le Sc(OH)_3$
- **15.** Select the **incorrect** statement:
  - (1) The higher oxidation state for d-block elements is most stable with F
  - (2) The bond strength order of the following ions is:  $Zn_2^{2+} > Hg_2^{2+} > Cd_2^{2+}$
  - (3) The ionic size of the following ions is:  $Mn^{2+} > Fe^{2+} > Co^{2+} > Ni^{2+}$
  - (4) Mn<sub>2</sub>O<sub>7</sub> exists but MnF<sub>7</sub> does not
- **16.** Select the correct statement:
  - (1) Zero and negative oxidation state of d-block metal ion is possible in their complex compound.
  - (2) Aquated Cu<sup>⊕</sup> cation undergo disproportionation due to hydration energy of Cu2+ is higher than that of Cu® which compensates first ionisation energy of Cu.

- (3) Zn gives  $H_2$  gas with dil. HCl and dil.  $H_2SO_4$  but gives NO<sub>2</sub>(g) with dil. HNO<sub>3</sub>
- (4) Covalent character is:  $HgCl_2 > CdCl_2 > ZnCl_2$

#### Colour

- 17. Which of the following compound is not coloured?
  - (1) Copper(II) sulphate
- (2) Zinc(II) chloride
- (3) Chromium(II) sulphate (4) Manganese(II oxalate)
- 18. Amongst,  $NiCl_4^{2-}$ ,  $Cu_2Cl_2$ ,  $ScF_6^{3-}$  and  $CoF_6^{3-}$ , the coloured species are: (1)  $ScF_6^{3-}$  and  $Cu_2Cl_2$  (2)  $ScF_6^{3-}$  and  $CoF_6^{3-}$  (3)  $Cu_2Cl_2$  and  $NiCl_4^{2-}$  (4)  $CoF_6^{3-}$ ,  $NiCl_4^{2-}$

- 19.  $K_3[Fe(CN)_6]$  is used in the detection of  $Fe^{2+}$  ion, which gives a blue colour solution. This colour is due to the formation of:
  - (1)  $Fe_{\Lambda}[Fe(CN)_{6}]_{3}$
- $(2) \text{ Fe}_{3} [\text{Fe}(\text{CN})_{6}]_{2}$
- (3) Fe[Fe(CN)<sub>6</sub>]
- $(4) K_2 Fe[Fe(CN)_6]$

## **Magnetic Properties**

- 20. Which of the following contains the maximum number of unpaired electrons?
  - (1) TiCl<sub>3</sub>
- (2) MnCl<sub>2</sub>
- (3)  $FeSO_4$
- (4) CuSO<sub>4</sub>
- 21. Among the following pairs of ions, the lower oxidation state in aqueous solution is more stable than the other in
  - $(1) \operatorname{Ti}^{\oplus}, \operatorname{Ti}^{3+}$
- $(2) Cu^{\oplus}, Cu^{2+}$
- (3)  $Cr^{2+}$ ,  $Cr^{3+}$
- $(4) V^{2+}, VO^{2+}$
- 22. Within each transition series, the oxidation states
  - (1) Decreases regularly in moving from left to right
  - (2) First increases till the middle of period and then decreases
  - (3) First decreases till the middle of period and then increases
  - (4) None of the trend is correct
- 23. In which of the following complexes the metal ion is in zero oxidation state?
  - (1)  $[Cu(NH_3)_4]Cl_5$
- (2)  $Zn_2[Fe(CN)_6]$
- $(3) \text{ Mn}_{2}(\text{CO})_{10}$
- (4)  $[Ag(NH_2)_2]C1$
- 24. In general the order of reactivity of halogens with transition
  - (1)  $F_2 > Cl_2 > Br_2 > I_2$ 
    - (2)  $F_2 < Cl_2 < Br_2 < I_2$
  - (3)  $F_2 < Cl_2 > Br_2 < I_2$
- (4)  $F_2 > I_2 > Br_2 > Cl_2$
- **25.** Select the incorrect statement:
  - (1) Orbital angular momentum for first series of transition metals is of no significance.
  - (2) The observed paramagnetism in 4f-block elements is due to both orbital motion of the electron and its spinning around its axis.
  - (3) Highest paramagnetism in 3d series in +1 oxidation state is shown by Mn<sup>+1</sup>.
  - (4) Highest paramagnetism in +2 oxidation state in 4d series is shown by Mo<sup>+2</sup>.
- 26. Out of the following, how many of them have magnetic moment value of  $\sqrt{48}$  BM
  - (i) Cr, (ii) Re, (iii) W, (iv) Mo, (v)  $\mathrm{Mn}^{+1}$ , (vi)  $\mathrm{Tc}^{+1}$ , (viii)  $\mathrm{Fe}^{+3}$
  - (1)5

(3) 3

(4)2

## Chemical Characteristics, KMnO<sub>4</sub> and K<sub>2</sub>Cr,O<sub>7</sub>

- 27. Which of the following cannot reduce the acidified solution of permanganate?
  - (1) (COOH)<sub>2</sub>
- (3) Nascent hydrogen
- (4)  $\overline{\text{Fe}^{2+}}$  ions
- 28. Which of the following can be employed for the conversion of potassium manganate to potassium permanganate?
  - $(1) O_{3}$

- (2) Cl<sub>2</sub>
- (3) Electrolysis
- (4) All
- 29. The blue colour produced on adding  $H_2O_2$  to acidifiedK<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> is due to the formation of
  - (1) CrO<sub>5</sub>
- (2) Cr<sub>2</sub>O<sub>2</sub>
- $(3) \operatorname{CrO}_{4}^{2}$

- 30. The equilibrium  $\operatorname{Cr}_2\operatorname{O}_7^{2-} \Longrightarrow 2\operatorname{Cr}\operatorname{O}_4^{2-}$ 
  - (1) Exists in acidic maximum
  - (2) Exists in basic medium
  - (3) Exists in neutral medium
  - (4) It does not exist
- 31. Which of the following compounds is used as the starting material for the preparation of potassium dichromate?
  - (1)  $K_2SO_4 \cdot Cr_2(SO_4)_3 \cdot 24H_2O$  (Chrome alum)
  - (2) PbCrO<sub>4</sub> (Chrome yellow)
  - (3) FeCr<sub>2</sub>O<sub>4</sub> (Chromite)
  - (4) PbCrO<sub>4</sub>PbO (Chrome red)
- 32. The image on an exposed and developed photographic film is due to
  - (1) AgBr

(2)  $[Ag(C_2O_3)_2]^{3+}$ 

(3) Ag

- 33. During titration, H<sub>2</sub>SO<sub>4</sub> is preferably used over HCl and HNO<sub>3</sub> to make the solution acidic because
  - (1) H<sub>2</sub>SO<sub>4</sub> is a strong oxidising agent and it reacts with KMnO<sub>4</sub> during titration
  - (2) Some KMnO<sub>4</sub> is consumed during the reaction with
  - (3)  $H_2SO_4$  does not react with  $KMnO_4$  or the reducing agent
  - (4)  $H_2SO_4$  can turn colourless  $KMnO_4$  to pink at the end
- 34. When  $KMnO_4$  is added to oxalic acid, the decolourisation is slow in the beginning 'but becomes instantaneous after sometime because
  - (1) Mn<sup>2+</sup> acts as autocatalyst
  - (2) CO<sub>2</sub> is formed as the product
  - (3) Reaction is exothermic
  - (4)  $MnO_4^{\Theta}$  catalyses the reaction
- 35. Which of the following oxides of manganese is amphoterical
  - $(1) \text{ MnO}_2$
- $(2) \text{ Mn}_{2}\text{O}_{3}$
- $(3) \text{ Mn}_2\text{O}_7$
- (4) MnO
- **36.** Number of moles of K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> reduced by one mole of Sn ion is
  - (1) 1/3

(2) 3

(3) 1/6

(4)6

melting point belongs to

(4) Oxidation states

6.56	Inorganic Chemistry					
	(1) Group 3	(2) Group 11	Co	mpounds of Transition	Elements	\
	(3) Group 6	(4) Group 12	Iro			
60.	The stability of particula	r oxidation state of a metal in	70.	<ul> <li>Important ore of iron is</li> </ul>		
	aqueous solution is determ			(1) Garnierite	(2) Pentalandite	
	(1) Enthalpy of sublimation	on of the metal		(3) Haematite	(4) Smaltite	
	(2) Ionisation energy		71.	. A compound of iron e	xists as a dimer in vapour state.	I.
	<ul><li>(3) Enthalpy of hydration</li><li>(4) All of these</li></ul>	of the metal ion		hygroscopic in nature acidic solution. The co	and dissolves in water giving he	lWO.
61		is not a condition for complex		$(1) \operatorname{Fe_3O_4}$	(2) $FeSO_4$	
01.	formation?	is not a condition for complex		(3) FeCl <sub>3</sub>	(4) FeO <sub>2</sub>	
	(1) Small atomic size		72.	. Which among FeO and	I Fe <sub>2</sub> O <sub>2</sub> is more basic?	
	(2) High nuclear charge			(1) FeO	2 3	
	(3) Variable oxidation stat	es		$(2) \operatorname{Fe}_2 O_3$		
	(4) Availability of vacant of			(3) Both have same bas	sic strength	
62	Which is not amphoteric?			(4) None of them is bas		
02.	(1) $Al^{3+}$	(2) $Cr^{3+}$	73	The colour of FeF <sub>3</sub> is		
	(3) $Fe^{3+}$	(4) $Zn^{2+}$	13.	(1) Brown	(2) Red brown	
(2				(3) Light green	(4) White	
03.	oxides?	react with which of the following	74	· 101 -		
	(1) CaO	(2) Na <sub>2</sub> O <sub>2</sub>	/4.	Iron is obtained on a la	2 3 -	
	(3) ZnO	$(4) \text{ Mn}_3 \text{O}_4$		(1) Reduction with Al	(2) Smelting with carbon	
64	Coinage metals show the	3 1	-	(3) Calcination	(4) Water gas	_
0.	(1) Typical elements	(2) Normal elements	75.		of $Fe(SCN)_3$ and $Fe(SCN)_4$	İS
	(3) Transitional elements	(4) Inert elements		destroyed by addition of		
65	When $(NH_4)_2CrO_2O_7$ is h			$(1) F^{\Theta}$	$(2) \text{ CN}^{\Theta}$	
0.5	(1) $N_2$	(2) $NO_2$		(3) SCN <sup>⊖</sup>	(4) Fe <sup>⊖</sup>	
	$(3) O_2$	$(4) \text{ Na}_2 \text{O}$	Co	pper		
66.	Which of the following o	_	76.	. On heating copper nitra	ite strongly the compound obtaine	d is
00.		$(2) \operatorname{Cr}_2 \operatorname{O}_3$		(1) Copper	(2) Copper oxide	
	$(3) \operatorname{CrO}_{5}$	(4) CrO <sub>3</sub>		(3) Copper nirtite	(4) Copper nitride	
67.	Select the incorrect staten	3	77.	. Which of the following	g is fool's gold?	
07.		e number of oxidation states than		(1) CuFeS <sub>2</sub>	(2) Cu(OH),	
	that of corresponding	lanthanides		$(3) \operatorname{Cu(OH)}_2 \cdot \operatorname{CuCO}_3$	(4) Cu <sub>2</sub> S	
		6 misch metal mixed with Mg	<b>78.</b>	. Bordeaux mixture cons	ists of lime and	
	(3) The size of lanthanide	s M <sup>3+</sup> ions increases as the atomic		$(1) \text{ FeSO}_4$	(2) $CuSO_4$	
	number of M increases	s		$(3) \operatorname{Cu(NO}_3)_2$	(4) AgNO <sub>3</sub>	
	(4) Electronic spectra of la	anthanide show very broad bands	79.	In vapour state Cu(NC	$(O_3)_2$ and $(CH_3COO)_4 \cdot 2H_2O =$	xist
<b>68.</b>	Select the incorrect statem			as	3/2	
	(1) Sphalerite is an ore of			(1) Dimer, monomer		
	(2) Terbium (Tb) has 4f	<sup>9</sup> 6s <sup>2</sup> and Gadolinium (Gd) has		(2) Monomer, dimer		
	4f' 5s' 6s' electronic	configuration. The spin magnetic		(3) Monomer, monome	r	
	moment of Tb <sup>3+</sup> is gre			(4) Dimer, Dimer		
		n densities except Th and Am.	80	Which compound is for	rmed when iron reacts with carbo	n?
	(4) Monazite is an ore of t			$(1) \operatorname{FeC}_2$	(2) Fe <sub>3</sub> C	
69.	Select incorrect statement			(3) $FeC_3$	(4) Fe <sub>2</sub> C	
		<sup>5</sup> and 5f <sup>8</sup> electronic configuration	Sil	ver:	-	
	are not known.	1.468 1	81.	Which of the following	g is known as WORM SILVER?	
		and 4f <sup>8</sup> electronic configuration		(1) AgCl		
	are not known.	de ara lass basis them		(2) A specific horn, type	e article made of silver	
	(3) Lanthanoid compound compounds.	ds are less basic than actinoid		$(3) Ag_2S$		
	•	ds have more tendency towards		(4) PbS containing trace	es of Ag <sub>2</sub> S	
(	complex formation.	is have more tendency towards				

It is always advisable not to cover egg yolk or mustard with silver cutlery because Silver reacts with water of egg yolk to form AgOH (1) Silver reacts with sulphur of egg yolk forming black

Silver reacts with egg yolk forming Ag<sub>2</sub>SO<sub>4</sub> which is a poisonous substance

Silver attracts UV light of the atmosphere, thereby spoiling the food.

giver halides are used in photography because they are

(1) Photosensitive

(2) Soluble in hyposolution

(3) Soluble in NH<sub>4</sub>OH

(4) Insoluble in acids

Which of the following is false?

(1) Molten lead and zinc are miscible.

(2) Silver is more soluble in molten zinc than lead.

(3) Zinc–silver alloy is volatile.

(4) Zinc-silver alloy is heavier and gets solidified later than

& AgNO3 gives red ppt. with

(1) NaI

(2) KC1

(3) NaNO<sub>2</sub>

(4) Na<sub>2</sub>CrO<sub>4</sub>

Percentage of gold in 21.6 carat gold is

(1) 21.8%

(2)90%

(3) 10%

(4)70%

J. Gold dissolves in aqua regia forming

 $(1) \operatorname{Au}(NO_3)_2$ 

(2) H[AuCl<sub>4</sub>]

(3) AuCl

(4) AuNO<sub>3</sub>

18. The process of extraction of Au and Ag ores is based on their solubility in

 $(1) NH_{2}$ 

(2) HCl

(3) HNO<sub>3</sub>

(4) KCN

Mich of the following is used as purgative in medicine?

(1) ZnCl<sub>2</sub>

(2) HgCl<sub>2</sub>

(3) Hg<sub>2</sub>Cl<sub>2</sub>

(4)  $ZnSO_4 \cdot 7H_2O$ 

M. The roasting of HgS in air produces

(l) HgO

(2) HgSO<sub>3</sub>

(3) HgSO<sub>4</sub>

(4) Hg

Which of the following is used as a white pigment?

 $(1) Z_{nO}$ 

(2) Na<sub>2</sub>ZnO<sub>2</sub>

(3) ZnS

(4) ZnCO<sub>3</sub>

Mercury (I) chloride sublimes, when this compound is heated and the vapours it gives off are cooled the substance collected consists of

(1) Mercury (II) chloride

(2) Mercury (I) and Mercury (II), chlorides

(3) Mercury (II) chloride and mercury

(4) Mercury

98. Which of the following is used for joining the broken pieces of glass and stones?

(1) Haematite

(2) Sindoor

(3) Massicot

(4) German silver

99. Which method is based on distribution principle?

(1) Mond's process

(2) Plattner's principle

(3) Glower's process

(4) Parke's process

**100.** Which of the following statements is wrong?

(1) An acidified solution of K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> liberates iodine from iodides

(2) In acidic solution dichromate ions are converted to chromate ions

(3) Ammonium dichromate on heating undergo exothermic decomposition to give Cr<sub>2</sub>O<sub>3</sub>

(4) Potassium dichromate is used as a titrant for Fe<sup>2+</sup> ions

101. When H<sub>2</sub>S gas is passed through an orange red solution (X), the solution turns milky. When an alkali is added to this orange red solution it turns yellow and on acidifying this yellow solution again turns orange red. X is

 $(1) K_2 CrO_4$ 

(2) KMnO<sub>4</sub>

(3) Na<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>

 $(4) K_2Cr_2O_7$ 

102. Which of the following statements is incorrect?

(1) Basic copper carbonate is CuCO<sub>3</sub>·Cu(OH),

(2) On strong heating potassium dichromate decomposes with evolution of oxygen

(3) CuS is white in colour

(4) KMnO<sub>4</sub> exists as dark purple black prismatic crystals

103. A man made white silvery metal, radioactive in nature has a strong tendency to form oxocations and complexes. It is used as a nuclear fuel in atomic reactors. The metal is a

(1) Lanthanide

(2) Actinide

(3) Transition metal

(4) Representative element

104. From a solution of CuSO<sub>4</sub>, the metal used to recover copper is

<b>6.58</b> Inorganic Chemistry			
(1) Na	(2) Ag	116. The correct formula of p	
(3) Hg	(4) Fe	$(1) \text{ HMnO}_4$	(2) HMnO <sub>5</sub>
105. Iron, once dipped in co	ncentrated H <sub>2</sub> SO <sub>4</sub> , does not displace	$(3) H_2MnO_4$	(4) H2MnO3
copper from copper sul		117. Which of the following state decomposition an heating	species undergo non-redor "
(1) It is less reactive that	an copper	decomposition an heating	g.
(2) A layer of sulphate	is deposited on it	$(1) SnSO_4$	$(2) H_2 C_2 O_4$
(3) An inert layer of iro	n oxide s deposited on it	(3) Na <sub>2</sub> HPO <sub>4</sub>	$(4) \operatorname{FeSO}_4$
(4) All valence electror	s of iron are consumed	118. Water soluble salt (X) is C. Products B and C are	heated into three products A
<b>106.</b> Which of the following precipitate with Ag <sup>⊕</sup> io		(A) is red in hot solution	The salt $(X)$ is:
$(1) SO_3^{2-}$	(2) Br <sup>⊖</sup>	$(1) \operatorname{FeC}_2 \operatorname{O}_4$	$(2) \operatorname{Hg(NO_3)_2}$
(3) $CrO_4^{2-}$	$(4) S_2 O_3^{2-}$	$(3) Pb(NO_3)_2$	(4) ZnSO <sub>4</sub>
4	gives oxygen on moderate heating is	119. Metal $\xrightarrow{\text{dil.}}$ Colour $\xrightarrow{\text{HNO}_3}$	less solutionaq. NaOH
(1) Zinc oxide	(2) Mercuric oxide	(M) excess	,
(3) Aluminium oxide	(4) Ferric oxide	white ppt. $\stackrel{\text{NaOH (aq)}}{\longrightarrow}$	Colourless solution
108. Identify the statement v	which is not correct regarding CuSO <sub>4</sub>		3074110[[
(1) It reacts with KI to		$\xrightarrow{H_2S}$ white ppt.	
(2) It reacts with KCl to	o give Cu <sub>2</sub> Cl <sub>2</sub>	Metal (M) is:	
	I and glucose to give Cu <sub>2</sub> O	(1) Sn	(2) Zn
(4) It gives CuO on stro	ong heating in air	(3) Pb	(4) Mg
109. KI and CuSO <sub>4</sub> solution	s when mixed give	120. Select incorrect statemen	
$(1) \operatorname{CuI}_2 + \operatorname{K}_2 \operatorname{SO}_4$	(2) $Cu_2I_2 + K_2SO_4$		relatively more stable than Ni
$(3) K_2 SO_4 + Cu_2 I_2 + I_2$	(4) $K_2SO_4 + CuI_2 + I_2$	compounds	y sale state than M
110. Bordeaux used a fungio	eide is a mixture of	(2) LiAlH <sub>4</sub> on hydrolysis	gives H <sub>2</sub>
(1) $CuSO_4 + Ca(OH)_2$ (3) $CuCO_3 + Cu(OH)_2$	(2) CaSO4 + Cu(OH)2 $(4) CuO + CaO$		can be done in the atmosphere
to its	tal which is liquid at 0°C. This is due		ion, with nitroprusside ion, to for mpound. In this reaction oxidation
(2) Low ionisation pote	energy and weakly metallic bond	_	avera of VCN
(3) High atomic weight		121. $CuSO_4(aq) \xrightarrow{H_2S} A -$	$\xrightarrow{\text{excess of KCN}} B + C.$
(4) High vapour pressur		The product B and C resp	pectively are:
112. Which one of the follow		(1) CuCN, (CN) <sub>2</sub>	(2) $Cu(CN)_2$ , $K_2S$
(1) It can evolve hydrog	8	-	(4) $[Cu(CN)_4]^{3-}$ , $(CN)_2$
(2) It is metal	en nom H <sub>2</sub> S	122. Consider the reaction,.	(9)[()41 )()
(3) It has high specific h	eat		2.37 . 37
(4) It is less reactive that		$2\text{CuX}_2 \xrightarrow{\text{Room}} 2\text{Cov}$	$\Delta uX + X_2$
113. Which compound is vol	•	$X^{\odot}$ ion is	
(1) MgCl <sub>2</sub>	(2) HgCl <sub>2</sub>	(1) $\text{Cl}^{\odot}$ , $\text{F}^{\odot}$	$(2) \operatorname{Cl}^{\odot}, \operatorname{Br}^{\odot}$
$(3) \operatorname{ZnCl}_{2}$	(4) None of these	(3) $F^{\ominus}$ , $Br^{\ominus}$	(4) $CN^{\odot}$ , $I^{\odot}$
L	ring pairs of substances on reaction		
will not evolve H <sub>2</sub> gas?	ing pairs of substances on reaction	Multiple Correct Answer	s Type
(1) Iron and $H_2SO_{4(aq)}$		General Properties and Elec	tronic Configuration
(2) Iron and steam		1. $dz^2$ orbital is involved	d in which of the follows
(3) Copper and HCl <sub>(g)</sub>	ahal	hybridisation?	
(4) Sodium and ethyl alc		$(1) sp^3d$	$(2) dsp^3$
_	s not the characteristic of zinc?	$(3) sp^3d^2$	$(4) d^2sp^3$
(1) It is volatile metal		2. $d_{xy}$ , $d_{yz}$ and $d_{xz}$ orbitals is a hybridication?	involved in which of the following
(2) It dissolves in alkali f	,	hybridisation?	
(3) It is brittle at very hig	h temperatures	-	

(2) sp<sup>3</sup>d (4) d<sup>3</sup>sp<sup>3</sup>

 $(1) dsp^2$ 

 $(3) sp^3d^3$ 

(3) It is brittle at very high temperatures

(4) Zinc dust is used as a reducing agent

orbital is involved in which of the following  $\int_{-\infty}^{(3)^{-2}} orbital$  is involved in which of the following hybridisation?

(1)  $sp^3d$  $(3) sp^3d^3$ 

 $(2) sp^3 d^2$ 

(4) None of these

Which of following is/are correctly matched?

(1) d-block element:

electronic configuration is

 $ns^{0-2}(n-1)d^{1-10}$ 

(2) p-block element:

electronic configuration is  $ns^{1-2} np^{1-6}$ 

(3) s-block element:

electronic configuration is  $ns^{1-2}$ 

(4) Ce

f-block's first member.

Which of the following is false?

(1)  $Cr^{2+}_{(g)}$  ion has greater magnetic moment as compared to  $Co^{3+}_{(g)}$ 

- (2) The magnitude of ionisation potential of iron anion (monoanion) would be equal to electron gain enthalpy of
- (3) Lanthanoids contraction is cause of lower IE of Pb than
- (4) If successive ionisation energy are 332, 738, 849, 4080, 4958 (in kJ/mol). Then this element can be of 15th group.
- 7. Which of the following represents the incorrect order of the properties indicated?

 $(1) \text{Ni}^{2+} > \text{Cr}^{2+} > \text{Fe}^{2+} > \text{Mn}^{2+} \text{ (size)}$ 

(2) Sc > Ti > Cr > Mn (size)

 $(3) \text{Ni}^{2+} < \text{Co}^{2+} < \text{Fe}^{2+} < \text{Mn}^{2+} \text{ (unpaired electron)}$ 

 $(4) H_3 AsO_4 > H_3 PO_4$  (acidic strength order)

8. What will be the correct representation of quantum numbers for the last electron entered into Ce?

n l m S (1)43 -3-1/2(2)43 0 -1/2(3)42 -3+1/2

(4)43 +2-1/2

9. The ability of d-block elements to form complexes is due to:

(1) Small and highly charged ions

(2) Vacant low energy orbitals to accept lone pair of electrons from ligands

(3) Low polarising power of cation

(4) None is correct

10. A transition element X has a configuration  $3d^4$  in its +3 <sup>0xidation</sup> state. Its atomic number is not

(1)25

(2)26

(3)22

(4) 19

11. The transition metals which do not form amalgams are

 $(1) Z_n$ (3) Cd

(2) Fe (4) Pt

(3) They show variable oxidation state

(4) They have two electrons in their outermost shells.

13. Which out of the following belong to 3*d*-series?

(1) Copper

(2) Cobalt

(3) Gold

(4) Silver

14. The elements which exist in the liquid state at room temperature are

(1) Na

(2) Br<sub>2</sub>

(3) Hg

(4) Ga

15. Which of the following represents the correct order of the properties indicated?

(1)  $Ni^{2+} > Cr^{2+} > Fe^{2+} > Mn^{2+}$  (size)

(2) Sc > Ti > Cr > Mn (size)

(3)  $Ni^{2+} < Co^{2+} < Fe^{2+} < Mn^{2+}$  (unpaired electron)

(4)  $Cr^{3+} > Cr^{2+}$  (magnetic moment)

**16.** The correct statement for d-block element is

(1) It shows magnetic property.

(2) It has variable valency.

(3) It has tendency of formation of coloured ions.

(4) It has complete *d*-orbitals.

17. Which is/are true statement?

(1) Ions of d-block elements are coloured due to d-d transition.

(2) Ions of f-block elements are coloured due to f-f transition.

(3)  $\left[\operatorname{Sc}(H_2O)_6\right]^{3+}$ ,  $\left[\operatorname{Ti}(H_2O)_6\right]^{4+}$  are coloured complexes.

(4) Cu<sup>⊕</sup> is colourless ion.

18. Select the correct statements:

(1) Oxides of transition metals are highly coloured (generally black).

(2) Alloy of transition metal has often high melting points.

(3) Oxides of transition elements are insoluble in water.

(4) Existence of Mn<sub>2</sub>O<sub>7</sub> is due to ability of oxygen to form  $p\pi$ - $p\pi$  multiple bonds to Mn

19. Select the correct statements:

(1) Mn<sup>3+</sup> and Cr<sup>3+</sup> are violet in colour.

(2) Melting points of alloys is less than their individual metals.

(3) Order of acidic character of oxides of Mn.

 $Mn_2O_7 > MnO_2 > Mn_2O_3 > Mn_3O_4 > MnO.$ (4)  $Mn^{\oplus}$ ,  $Re^{+1}$  and  $Mn^{2+}$  have 6 unpaired  $e^{-t}$ s

20. Select the correct statements:

An elements of 3d transition series shows two oxidation states x and y, differ by two units then.

(1) Compounds in O.S., x are ionic if x > y

(2) Compounds in O.S., y are covalent if x < y

(3) Compounds in O.S., x are ionic if x < y

(4) Compounds in O.S., y are covalent if y < x

## 6.60 Inorganic Chemistry

- **21.** Select the correct statements:
  - (1) "Spitting of silver" can be prevented by covering the surface of molten Ag with charcoal.
  - (2) Order of paramagnetic character is: Cr > Fe > Zn
  - (3) An alloy is a blend of metals prepared by mixing the compounds.
  - (4) The melting and boiling points of Zn, Cd and Hg are high.
- 22. Select the correct statements:
  - (1) There is a very small difference in the melting point of Cr and Zn
  - (2) Chromium is a typical hard metal while mercury is a liquid.
  - (3) Pt<sup>4+</sup> compounds are more stable than Ni<sup>4+</sup>compounds.
  - (4) Ni<sup>2+</sup> compounds are more stable than Pt<sup>2+</sup> compounds.

#### Colour

- **23.** Which one of the following ionic species will not impart colour to an aqueous solution?
  - $(1) \text{ Ti}^{4+}$

- (2) Cu<sup>⊕</sup>
- $(3) Zn^{2+}$

- $(4) Cr^{3+}$
- 24. The colour of the transition metal ions is due to
  - (1) d–d transition
- (2) Charge transfer
- (3) Change in the geometry (4) None

#### **Magnetic Properties**

- **25.** Out of [Fe(CN)<sub>6</sub>]<sup>4-</sup>, [Ni(CN)<sub>4</sub>]<sup>2-</sup>, and [Ni(CO)<sub>4</sub>]: select the **incorrect** statement(s):
  - (1) All have identical geometry
  - (2) All are paramagnetic
  - (3) All are diamagnetic
  - (4)  $[Fe(CN)_6]^4$  is diamagnetic but  $[Ni(CN)_4]^{2-}$  and  $[Ni(CO)_4]$  are paramagnetic

## KMnO<sub>4</sub> and K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>

- **26.** Which is true statement about KMnO<sub>4</sub>?
  - (1) Its solution is unstable in acidic medium.
  - (2) It has purple colour.
  - (3) MnO<sub>4</sub><sup>⊖</sup> changes to Mn<sup>2+</sup> in basic solution.
  - (4) It is self-indicator in  $Fe^{2+}$  or  $C_2O_4^{2-}$  titration.
- 27. Potassium manganate (K<sub>2</sub>MnO<sub>4</sub>) is formed when
  - (1) Chlorine is passed through aqueous KMnO<sub>4</sub> solution
  - (2) Manganese dioxide is fused with potassium hydroxide in air
  - (3) Formaldehyde reacts with potassium
  - (4) potassium permanganate reacts with H<sub>2</sub>SO<sub>4</sub>
- **28.** Cl<sub>2</sub> gas is obtained by various reactions select the reactions from the following(s):
  - (1) KMnO<sub>4</sub> + conc. HCl  $\xrightarrow{\Delta}$
  - (2) KCl +  $K_2Cr_2O_7$  + conc.  $H_2SO_4 \xrightarrow{\Delta}$
  - (3) MnO<sub>2</sub> + conc. HCl  $\xrightarrow{\Delta}$
  - (4) KCl +  $F_2 \xrightarrow{\Delta}$
- **29.** In the iodometric estimation in the laboratory which process is involved?

- (1)  $\operatorname{Cr_2O_7}^{2-} + \operatorname{H}^{\oplus} + \operatorname{I}^{\ominus} \longrightarrow 2\operatorname{Cr}^{3+} + \operatorname{I}_2$  $\operatorname{I}_2 + \operatorname{S}_2\operatorname{O}_3^{2-} \longrightarrow \operatorname{S}_4\operatorname{O}_6^{4-} + \operatorname{I}^{\ominus}$
- $(2) \operatorname{MnO}_{4}^{\ominus} + \operatorname{H}^{\oplus} + \operatorname{I}^{\ominus} \longrightarrow \operatorname{Mn}^{2+} + \operatorname{I}_{2}$   $\operatorname{I}_{2} + \operatorname{S}_{2} \operatorname{O}_{3}^{\ominus} \longrightarrow \operatorname{S}_{4} \operatorname{O}_{6}^{2-} + \operatorname{I}^{\ominus}$
- (3)  $\operatorname{MnO_4}^{\ominus} + \operatorname{OH}^{\ominus} + \operatorname{I}^{\ominus} \longrightarrow \operatorname{MnO_2} + \operatorname{I_2}$   $\operatorname{I_2} + \operatorname{S_2O_3}^{2-} \longrightarrow \operatorname{S_4O_6}^{2-} + \operatorname{I}^{\ominus}$
- (4)  $\operatorname{Cr_2O_7}^{2-} + \operatorname{OH}^{\Theta} + \operatorname{I}^{\Theta} \longrightarrow 2\operatorname{Cr}^{3+} + \operatorname{I}_2$  $\operatorname{I}_2 + \operatorname{S}_2\operatorname{O}_3^{2-} \longrightarrow \operatorname{S}_4\operatorname{O}_6^{2-} + \operatorname{I}^{\Theta}$
- **30.** Which reagents can convert Mn<sup>2+</sup> to MnO<sub>4</sub>
  - (1)  $S_2O_8^{2-}/H^{\oplus}$
- (2)  $PbO_2/H^{\oplus}$
- (3) BiO<sub>3</sub><sup>⊙</sup>/H<sup>⊕</sup>
- (4) H<sub>2</sub>O<sub>2</sub>/H<sup>⊕</sup>
- 31. Select the correct statements
  - (1) When CO<sub>2</sub> is passed into aqueous solution of CrO<sub>2</sub> CrO<sub>5</sub> is formed
  - (2) When CO<sub>2</sub> is passed into MnO<sub>4</sub><sup>2-</sup> (green) solution it turns purple and a brown precipitate of MnO<sub>2</sub> is formed
  - (3) The yellow colour of  $CrO_4^{2-}$  is due to *d-d* transition
  - (4) The yellow colour of  $CrO_4^{2-}$  is due to charge transfer.
- 32. Select the correct statements:
  - (1)  $\rm MnO_2$  dissolves in conc. HCl but does not form  $\rm Mn^{4-}$   $\rm log$
  - (2) MnO<sub>4</sub><sup>2-</sup> is strongly oxidizing and stable only in very strong alkali.
  - (3) KMnO<sub>4</sub> does not act as oxidizing agent in basic medium
  - (4) Decomposition of acidic KMnO<sub>4</sub> is not catalysed by sunlight.

## f-block

- 33. Select the correct statements:
  - (1) Sm<sup>2+</sup>, Eu<sup>2+</sup> and Yb<sup>2+</sup> are good oxidizing agent.
  - (2) Zr and Hf shows similar properties
  - (3) La (OH)<sub>3</sub> is the strongest base than the other lanthanum hydroxides.
  - (4) Magnetic susceptibility values of actinides are greater than lanthanides.
- **34.** Select the correct statements:
  - (1) Ce<sup>3+</sup> can be easily oxidized to Ce<sup>4+</sup>
  - (2) Chemical properties of all the lanthanoids are quite similar.
  - (3) Gd<sup>3+</sup> and Lu<sup>3+</sup> are stable.
  - (4) La<sup>4+</sup> exists.

## Miscellaneous Compounds

- **35.** Which of the following statements are correct with reference to the ferrous and ferric ions?
  - (1) Fe<sup>3+</sup> gives brown colour with potassium ferricyanide.
  - (2) Fe<sup>2+</sup> gives blue precipitate with potassium ferricyanide.
  - (3) Fe<sup>3+</sup> gives red colour with potassium thiocyanate.
  - (4) Fe<sup>2+</sup> gives brown colour with ammonium thiocyanate
- **36.** The aqueous solution of the salt will be coloured in the case of
  - $(1) \operatorname{Zn}(\operatorname{CO}_3)_2$
- (2) LiNO<sub>3</sub>
- (3) Co(NO<sub>3</sub>)<sub>2</sub>
- (4) CrCl<sub>3</sub>

 $\int_{M}^{\infty} |fe(CN)_{5}(NO)|^{2-}$ , Fe has +2 state. It cannot be decided by Magnetic measurement (2) Colligative property

(3) Colour Which one of the following statements is/are correct?

Zinc dissolves in sodium hydroxide solution.

(I) Carbon monoxide reduces iron(III) oxide to iron. (3) Mercury(II) iodide dissolves in excess of potassium

iodide solution.

(4) Tin(IV) chloride is made by dissolving tin solution in concentrated hydrochloric acid.

& Select the correct statements

ZnCO<sub>3</sub> and CuO give metal on heating.

When CN<sup>©</sup> ion is added to CuSO<sub>4</sub>, CN<sup>©</sup> ion acts as oxidizing agent.

(3) AgF is soluble in H<sub>2</sub>O

(4) Silver halides dissolve in thiosulphate and cyanide solution.

The species that undergo disproportionation in basic medium

(1) C10<sub>4</sub>

(2) MnO<sub>4</sub><sup>2-</sup> (4) NO<sub>2</sub>

(3) Cl<sub>2</sub>

## linked Comprehension Type



## Paragraph 1

recolours of the transition metal are due to d-d excitation. The argy required for d-d electron excitation is available in the

instition metal ions have the tendency to absorb certain radiations in the visible region and exhibit the complementary

transition metal ions which have completely filled d-orbitals a colourless as the excitation of electron or electrons is not Massible within d-orbitals. The transition metal ions which have impletely empty d-orbitals are also colourless. In KMnO<sub>4</sub> and LCr<sub>2</sub>O<sub>7</sub>, there are no unpaired electrons at the central atom they are deep in colour. The colour of these compounds due to charge transfer spectrum. For example, in MnO<sub>4</sub> electron is momentarily transferred from O to the metal thus oxygen changes from  $O^{2-}$  and  $O^{\Theta}$  manganese from

1. Which of the following is paramagnetic as well as coloured

(1) Cu<sup>⊕</sup>

(2)  $Cu^{2+}$ 

 $(3) Sc^{3+}$ (4)  $Zn^{2+}$ 

<sup>1</sup>. Which is a coloured ion?

(2)  $[Cu(CN)_4]^{3-}$ (4)  $[Sc(H_2O)_6]^{3+}$ 

(1)  $[Cr(H_2O)_6]^{3+}$ (3)  $[Ti(H_2O)_6]^{4+}$ 

Select the correct statement: (1) Colour of the transition metal ion arises due to d-d

(2) Colour of certain oxysalts of transition metals is due to charge transfer.

(3) Both are correct.

(4) None is correct

- 4. Which of the following compounds is(are) coloured due to charge transfer spectra and not due to d-d transitions?
  - $(1) \text{ KMnO}_4$

(2) K<sub>2</sub>CrO<sub>4</sub>

(3) CrO<sub>3</sub>

- (4) All of these
- 5.  $K_2Cr_2O_7$  gives coloured solution in water. The colour is due
  - (1) *d*–*d* transition in Cr-atoms
  - (2) Presence of unpaired electron in d-orbital of oxygen
  - (3) Charge transfer from 0 to Cr
  - (4) None of the above

#### Paragraph 2

KMnO<sub>4</sub> is prepared from the mineral pyrolusite, MnO<sub>2</sub> (deep purple colour). It acts as an oxidising agent in the neutral, alkaline as well as acidic medium. In acidic medium, it is used in volumetric analysis for estimation of  $\mathrm{Fe^{2^+}}$ ,  $\mathrm{Cr_2O_4^{2^-}}$  salts etc.

The titrations are carried out in presence of H<sub>2</sub>SO<sub>4</sub>. However, before using it as a titrant, it is first standardised with standard oxalic acid solution or Mohr's salt solution. In one of the experiments on titration 26.8 g of dry pure sodium oxalate  $(Mw = 134 \text{ g mol}^{-1})$  was dissolved in 1L of distilled water and then 100 mL of 2M H<sub>2</sub>SO<sub>4</sub> were added. The solution was cooled. Now to this solution, 0.1M KMnO<sub>4</sub> solution was added till a very faint pink colour persisted.

- 6. The purple colour of KMnO<sub>4</sub> is due to
  - (1) Incomplete d-subshell
  - (2) Ionic nature of KMnO<sub>4</sub>
  - (3) Charge transfer
  - (4) Resonance in  $MnO_4^{\ \Theta}$  ion
- 7. Mohr's salt, FeSO<sub>4</sub>·(NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>·6H<sub>2</sub>O, is preferred over FeSO<sub>4</sub>·7H<sub>2</sub>O for standardisation of KMnO<sub>4</sub> solution because
  - (1) Mohr's salt is a double salt while ferrous sulphate is a single salt.
  - (2) Mohr's salt is not hygroscopic but FeSO<sub>4</sub>·7H<sub>2</sub>O is hygroscopic.
  - (3) Mohr's salt contains only ferrous ions whereas ferrous sulphate contains some ferric ions.
  - (4) Mohr's salt solution can be titrated even in the absence of  $H_2SO_4$ .
- 8. When pyrolusite is fused with KOH and KClO<sub>3</sub>, we get
  - $(1) \text{ KMnO}_4$
- $(2) K_2 MnO_4$
- (3) Both KMnO<sub>4</sub> and K<sub>2</sub>MnO<sub>4</sub>
- (4) None of these
- 9. If 0.1 M K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> solution were used in place of 0.1 M KMnO<sub>4</sub> in presence of H<sub>2</sub>SO<sub>4</sub> in each case, the volume of 0.1 M K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> solution used would be
  - (1) 200 mL
- (2) 400 mL
- (3) 333.3 mL
- (4) 666.6 mL
- 10. If instead of H<sub>2</sub>SO<sub>4</sub>, HCl or HNO<sub>3</sub> of suitable concentration were used, the volume of KMnO<sub>4</sub> solution used would have
  - (1) Less in case of HCl but more in case of HNO<sub>3</sub>
  - (2) More in case of HCl but less in case of HNO<sub>3</sub>
  - (3) More in both cases
  - (4) Less in both cases

- 11. The volume of KMnO<sub>4</sub> solution that must have been added to obtain the faint pink colour at the end point must be
  - (1) 100 mL
- (2) 200 mL
- (3) 400 mL
- (4) 800 mL

## Paragraph 3

Transition metals and many of their compounds show paramagnetic behaviour where there are unpaired electron or electrons. The magnetic moment arises from the spin and orbital motions in ions or molecule. Magnetic moment of n unpaired electrons is given as

$$\mu = \sqrt{n(n+2)}$$
 Bohr Magneton

Magnetic moment increases as the number of unpaired electrons increases.

- 12. Which among the following ions has maximum value of magnetic moment
  - $(1) Cu^{2+}$

 $(3) Cr^{2+}$ 

- 13. Increasing value of magnetic moments of
  - (I)  $[Fe(CN)_6]^{4-}$  (II)  $[Fe(CN)_6]^{3-}$ , (III)  $[Cr(NH_3)_6]^{3+}$ ,
  - (IV)  $[Ni(H_2O)_4]^{2+}$  is:
  - (1) I < II < III < IV
- (2) IV < III < II < I
- (3) II < III < I < IV
- (4) I < II < IV < III
- 14. In 3d series the maximum magnetic moment is shown by
  - (1) Sc

(2) V

(3) Cr

- (4) Fe
- 15. Magnetic moments of Cr (Z = 24),  $Mn^{\oplus}$  (Z = 25) and  $Fe^{2+}$  (Z = 26) are x, y and z respectively. Which of the following order is correct?
  - (1) x < y < z
- (2) x = y < z
- (3) z < x = y
- (4) x = y = z
- 16. There are three unpaired electrons in  $[Co(H_2O)_6]^{2+}$ and calculated value of magnetic moment on the basis of  $\sqrt{n(n+2)}$  formula is 3.87 BM which is lower than the experimental value of 4.40 BM. The reason for this difference is due to
  - (1) Increase in number of unpaired electrons during determination
  - (2) Some contribution of the orbital motion of the electrons to the magnetic moment
  - (3) d–d transition
  - (4) Experimental error
- 17. Magnetic moment of  $[Ni(CN)_4]^{2-}$  is zero but that of  $[Ni(H_2O)_4]^{2+}$  is 2.83 BM. It is because of:
  - (1) CN<sup>©</sup> is a strong ligand making two unpaired electrons in Ni<sup>2+</sup> to pair up, while in [Ni(H<sub>2</sub>O)<sub>4</sub>]<sup>2+</sup> two electrons remain unpaired as H<sub>2</sub>O is a weak ligand
  - (2) Different oxidation state of Ni in two complexes
  - (3) Both (a) and (b)
  - (4) None of the above

#### Paragraph 4

Photography is based on the nature of silver halides. Except AgF. the silver halides are photosensitive. These undergo decomposition in light and turn black due to formation of free silver.

$$2AgBr \xrightarrow{Light} 2Ag + Br_2$$

The photography films are prepared by adding 20% aqueous to NH Br solution containing pelating pelatin The photography man solution of AgNO<sub>3</sub> to NH<sub>4</sub>Br solution containing gelatin. When which amplifying gets affected and a latest when solution of Agino3 to 11-4 such a film is exposed, emulsion gets affected and a latent  $im_{age}$ 

When this exposed film or plate is dipped in a developer which when this exposed most during exposure contains a reducing agent, the parts affected most during exposure which are reduced to the maximum. The image becomes visible. It is called a negative. The remaining sensitive emulsion on the negative is removed by dissolving it in hypo solution (fixer) Finally, a positive of the negative already prepared is  $made_{00}$ silver bromide paper.

- 18. The compound formed on the unexposed photographic film or plate is
  - (1) Silver nitrate
- (2) Ammonium bromide
- (3) Diammine silver bromide (4) Silver bromide
- 19. The exposed part of the film or plate after developing contains
  - (1) Silver metal
- (2) Silver oxide
- (3) Silver bromide
- (4) Silver nitrate
- 20. Silver halides are used in photography because these compounds
  - (1) Are insoluble in water
  - (2) Are affected by light
  - (3) Are soluble in ammonia solution
  - (4) Easily stick on the surface of photographic plate or film
- 21. The solution of the developer consists of
  - (1) Alkaline solution of pyrogallol
  - (2) Alkaline solution of quinol
  - (3) Either (a) or (b)
  - (4) Neither (a) nor (b)
- 22. Silver bromide dissolves in hypo solution forming:
  - (1) Ag<sub>2</sub>S<sub>2</sub>O<sub>3</sub>
- (2) Ag<sub>2</sub>S
- $(3) \text{ Na}_3[\text{Ag}(SO_3)_2]$
- (4) NaAgS<sub>2</sub>O<sub>3</sub>

#### Paragraph 5

In any transition series, from left to right, the d-orbitals are progressively filled and their properties vary accordingly.

- 23. In the second transition series, the largest number of oxidation states are shown by
  - (1) Tc

- (2) Ru
- (3) Rh

- (4) Pd
- 24. Which element do you expect to have the smallest atomic radius?
  - (1) La

(2) Zn

(3) Sc

- (4) Hg
- 25. Which element do you expect to have the highest melting point?
  - (1) La

(2) W

(3) Pt

- (4) Os
- 26. Which of the following pair of compounds is expected 10 exhibit same colour in aqueous solution?
  - (1) FeCl<sub>2</sub>, CuCl<sub>2</sub>
- (2) VOCl<sub>2</sub>, CuCl<sub>2</sub>
- (3) VOCl<sub>2</sub>, FeCl<sub>2</sub>
- (4) FeCl<sub>2</sub>, MnCl<sub>2</sub>

which of the following is the correct order of second in the correct order or second in the correct order of second in the correct order or ord

(1) V > Cr > Mn

(2)  $V < C_r < M_n$ 

(3) V < Cr > Mn

(4) V > Cr < Mn

pragraph 6 prepries with Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>) in acidic, strongly basic and aqueous of MnO<sub>4</sub> reacts with 100 mL of KMnO<sub>4</sub> reacts with 100 mL of MnO<sub>4</sub> reacts with 100 mL of 0.1 M acidic, basic and neutral media in acidic, basic and neutral media.

the molarity (M) of KMnO<sub>4</sub> solution in the acidic medium

(1) 0.2 M

(2) 0.02 M

(3) 0.4 M

(4) 0.04 M

The molarity (M) of KMnO<sub>4</sub> solution in basic medium is:

(1) 0.8 M

(2) 0.08 M

(3) 0.26 M

(4) 0.026 M

The molarity (M) of KMnO<sub>4</sub> in aqueous medium is

(1) 0.8 M

(2) 0.08 M

(3) 0.26 M

(4) 0.026 M

The molality (m) of KMnO<sub>4</sub> in the acidic medium is Density of KMnO<sub>4</sub> solution = 1.58 g mL<sup>-1</sup> Mw(KMnO<sub>4</sub>)

 $=158 \text{ g mol}^{-1}$ )

(2) 0.25

(1) 0.025 (3) 0.12

(4) 0.012

# Natrix Match Type

section contains questions each with two columns-I and II. the items given in column I with that in column II.

#### Match the column.

	Column I (Metal ion)		Column II (Magnetic moment) ((2)M.)
2.	Cr <sup>3+</sup>	p.	$\sqrt{35}$
b.	Fe <sup>2+</sup>	q.	$\sqrt{30}$
c,	Ni <sup>2+</sup>	r.	$\sqrt{24}$
d,	Mn <sup>2+</sup>	s.	$\sqrt{15}$
		t.	$\sqrt{8}$

# Match the column.

	Column I		Column II
a,	Ni	p.	Elements having same number of unpaired electron in their dispositive in column I
b.	Na	q.	At least 13 electrons are having magnetic quantum number 'zero'
c.	Mn	r.	Atom is paramagnetic
d.	Pd	s.	Element is not transition element
		t.	Element having pseudo inert gas configuration in its dipositive cation

#### 3. Match the column.

	Column I (Property)	Column II (Transition elements)				
а.	Highest oxidation state	p.	Cr			
b.	Highest density	q.	Os			
c.	Element with maximum unpaired electrons	r.	Тс			
d.	Radioactive transition element	S.	Ru			

#### 4. Match the column.

	Column I		Column II			
a.	K <sub>2</sub> MnO <sub>4</sub>	p.	Transition element in +6 oxidation state			
b.	KMnO <sub>4</sub>	q.	Paramagnetic			
c.	K <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub>	<b>r.</b>	Manufactured from pyrolusite ore			
d.	K <sub>2</sub> CrO <sub>4</sub>	s.	Manufactured from chromite ore			

## 5. Match the column.

	Column I (Alloys)		Column II (Constituents)				
a.	Gun metal	p.	Pb + Sn				
b.	German silver	q.	Cu + Sb + Zn				
c.	Brass	r.	Cu + Zn				
d.	Solder	s.	Cu + Zn + Ni				

## 6. Match the column.

	Column I		Column II
a.	Bayer's reagent	p.	$CuSO_4 + Ca(OH)_2$
b.	Bordeaux mixture	q.	1% alkaline KMnO <sub>4</sub>
c.	Nessler's reagent	r.	Detection of unsaturation in organic compounds

## 7. Match the column.

Column I		Column II		
a.	Corrosive sublimate	p.	A white pigment	
b.	Calomel	q.	HgCl <sub>2</sub>	
c.	Lithopone	r.	ZnSO <sub>4</sub> ·5H <sub>2</sub> O	
d.	ZnO	s.	BaSO <sub>4</sub> + ZnS	
e.	White vitriol	t.	Hg <sub>2</sub> Cl <sub>2</sub>	

### 8. Match the column.

Column I			Column II		
a.	Rinmann's green	p.	Red form of HgS		
b.	Pharash's serpent	q.	AgNO <sub>3</sub>		
c.	Lunar caustic	r.	Cobalt zincate		
d.	Vermilion	s.	Hg(CNS) <sub>2</sub>		
e.	Verdigris	t.	Basic copper acetate		

## 9. Match the column.

	Column I	拉程	Column
a.	Tenorite	p.	Mixture of copposite sulphide and r
b.	Parke's process	q.	Black oxide of
c.	Deacon's process	r.	Silver
d.	Matte	S.	Impure copper
e.	Blister copper	t.	Cupric chloride

## 10. Match the items given in Column I with that in Column II and III.

Column I Compound		Column II Characteristics (I)			Column III
				Characteristics (II)	
a.	KMnO <sub>4</sub>	i.	$KMnO_4 \xrightarrow{\Delta} \dots \dots + MnO_2 + O_2$ Blackish brown	p.	Dark green
b.	K <sub>2</sub> MnO <sub>4</sub>	ii.	Prepared from pyrolusite ore.	q.	Oxidising agent in acidic medium
c.	K <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub>	iii.	It oxidises I <sup>⊕</sup> to IO <sub>3</sub> <sup>⊕</sup> in basic medium	r.	Orange red colour changes to yellow in basic medium
d.	K <sub>2</sub> CrO <sub>4</sub>	iv.	Prepared from chromite ore.	s.	Yellow colour changes to orange red in acidic medium

## 11. Match the items given in Column I with that in Column II and III.

Column I Compound		Column II Characteristics (I)			Column III	
					Characteristics (II)	
a.	Calomel	i.	HgCl <sub>2</sub>	p.	Ionic and gives 3 ions in aqueous solution	
b.	Corrosive sublimate	ii.	It turns black with NH <sub>3</sub>	q.	Test for NH <sub>4</sub> <sup>⊕</sup> ions	
c.	Nessler's reagent	iii.	Hg <sub>2</sub> Cl <sub>2</sub>	r.	Used in making ink.	
d.	Lunar caustic	iv.	Alkaline solution of K <sub>2</sub> [HgI <sub>4</sub> ]	s.	Covalent and poisonous. Its antidote is white of an egg	
		v.	AgNO <sub>3</sub>			

## **Numerical Value Type**



- 1. What is the value of x in the following equation.  $Cr_2O_7^{2-} + 8H^{\oplus} + xS_2O_3^{2-} \longrightarrow 2Cr^{3+} + 3SO_4^{2-} + 3S + 4H_2O_3^{2-}$
- 2. What is the oxidation states of Cr in butterfly structure.
- 3. What is the value of x in the following equation:  $2MnO_4^{\ominus} + 3Mn^{2+} + 2H_2O \longrightarrow xMnO_2 + 4H^{\oplus}$
- **4.** Out of the following, how many oxides are acidic. MnO, Mn<sub>2</sub>O<sub>3</sub>, MnO<sub>2</sub>, MnO<sub>3</sub>, Mn<sub>2</sub>O<sub>7</sub>
- Out of the following, how many of them have magnetic moment value √24 BM.
   Ti<sup>2+</sup>, Ti<sup>3+</sup>, V<sup>2+</sup>, Cr<sup>2+</sup>, Cr<sup>3+</sup>, Mn<sup>2+</sup>, Fe<sup>2+</sup>

6. Out of the following how many of them are coloured compounds:

MnO<sub>4</sub><sup>$$\Theta$$</sup>, Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup>, CrO<sub>4</sub><sup>2-</sup>, Sc<sup>3+</sup>, Ti<sup>4+</sup>, Zn<sup>2+</sup>, Mn<sup>3+</sup>, Cu<sup>2+</sup>, Fe<sup>2+</sup>, Fe<sup>3+</sup>

- 7. Out of the following how many oxides are basic. TiO, Sc<sub>2</sub>O<sub>3</sub>, Ti<sub>2</sub>O<sub>3</sub>, VO, V<sub>2</sub>O<sub>5</sub>, CrO<sub>3</sub>, Cr<sub>2</sub>O<sub>3</sub>, CuO, TiO<sub>2</sub>
- 8. What is the value of x in the Wilkinson's catalyst [RhCl (Ph<sub>3</sub>P)x] which is used as a homogenous catalyst the hydrogenation of alkene.
- 9. How many of the transition elements are called coinage metals?
- 10. How many of the transition elements are called platinum metals?

# Archives

# JEE MAIN

# Gingle Correct Answer Type

knowing that the chemistry of lanthanoids (Ln) is dominated knowing by its +3 oxidation state, which of the following statements is incorrect?

Because of the large size of the Ln (III) ions the bonding in its compounds is predominantly ionic in character

- (2) The ionic sizes of Ln (III) decrease in general with increasing atomic number
- (3) Ln (III) compounds are generally colorless
- (4) Ln (III) hydroxides are mainly basic in character

## (AIEEE 2009)

- In context with the transition elements, which of the following statements is incorrect?
  - (1) In addition to the normal oxidation state, the zero oxidation state is also shown by these elements in complexes.
  - (2) In the highest oxidation states, the transition metal shows basic character and forms cationic complexes
  - (3) In the highest oxidation states of the first five transition elements (Sc to Mn), all the 4s and 3d electrons are used for bonding
  - (4) Once the  $d^5$  configuration is exceeded, the tendency to involve all the 3d electrons in bonding decreases.

## (AIEEE 2009)

- 3. The correct order of  $E^{\circ}_{M^{2+}/M}$  values with negative sign for the four successive elements Cr, Mn, Fe, and Co is
  - (a) Mn > Cr > Fe > Co
- (b) Cr > Fe > Mn > Co
- (c) Fe > Mn > Cr > Co
- (d) Cr > Mn > Fe > Co

#### (AIEEE 2010)

- 4. In context of the lanthanoids, which of the following statements is not correct?
  - (1) There is a gradual decrease in the radii of the members with increasing atomic number in the series.
  - (2) All the members exhibit +3 oxidation state.
  - (3) Because of similar properties the separation of lanthanoids is not easy.
  - (4) Availability of 4f electrons results in the formation of compounds in +4 state for all the members of the series.

#### (AIEEE 2011)

- 5. The outer electron configuration of Gd (At. no. 64) is
  - (1)  $4f^3$ ,  $5d^5$ ,  $6s^2$
- $(2)4f^8, d^0, 6s^2$
- (3)  $4f^4$ ,  $5d^4$ ,  $6s^2$
- $(4)4f^7, 5d^1, 6s^2$

## (AIEEE 2011)

- 6. Which of the following arrangements does not represent the correct order of the property stated against it?
  - (1)  $V^{2+} < Cr^{2+} < Mn^{2+} < Fe^{2+}$ : paramagnetic behavior
  - (2)  $Ni^{2+} < Co^{2+} < Fe^{2+} < Mn^{2+}$ : ionic size
  - $^{(3)}$ Co<sup>3+</sup> < Fe<sup>3+</sup> < Cr<sup>3+</sup> < Sc<sup>3+</sup>: stability in aqueous solution

(4)  $Sc \le Ti \le Cr \le Mn$ : number of oxidation states

(JEE Main 2013)

- 7. The colour of  $KMnO_4$  is due to
  - (1)  $M \rightarrow L$  charge transfer transition
  - (2) d d transition
  - (3)  $L \rightarrow M$  charge transfer transition
  - (4)  $\sigma \sigma^*$  transition

(**JEE Main 2015**)

## JEE ADVANCED

## Single Correct Answer Type

- 1. The colour of light absorbed by an aqueous solution of CuSO<sub>4</sub> is
  - (1) Orange red
- (2) Blue green
- (3) Yellow
- (4) Violet (IIT-JEE 2012)
- 2. In the cyanide extraction process of silver from argentite ore, the oxidising and reducing agent respectively are
  - $(1) O_2$  and  $CO_2$
- (2)  $O_2$  and Zn dust
- (3) HNO<sub>3</sub> and CO
- (4) HNO<sub>3</sub> and Zn dust

(IIT-JEE 2012)

- 3. Four successive members of first row transition element are listed below. Which one of them is expected to have highest  $E_{M^{3+}/M^{2+}}^{\Theta}$  value ?
  - (1) Mn (Z = 25)
- (2) Fe (Z = 26)
- (3) Co (Z = 27)
- (4) Cr(Z = 24)

(JEE Advanced 2013)

- 4. Which of the following statements about the interstitial compounds is incorrect?
  - (1) They are much harder than the pure metal.
  - (2) They have higher melting points than the pure metal.
  - (3) The retain metallic conductivity.
  - (4) They are chemically reactive.
- (JEE Advanced 2013)
- 5. KMnO<sub>4</sub> can be prepared from K<sub>2</sub>MnO<sub>4</sub> as per the reaction:  $3MnO_4^{2-} + 2H_2O \Longrightarrow 2MnO_4^{\odot} + MnO_2 + 4OH^{\odot}$ The reaction can go the completion by removing  $OH^{\Theta}$  ions
  - by adding (1) CO<sub>2</sub>
- (2) SO<sub>2</sub>

(3) HCl

(4) KOH

(JEE Advanced 2013)

- 6. A magnetic moment of 1.73 B.M. will be shown by one among the following:
  - $(1) \operatorname{TiCl}_{4}$

- $(2) [CoCl_6]^{4-}$
- (3)  $\left[ \text{Cu(NH}_3)_4 \right]^{2+}$
- (4)  $[Ni(CN)_4]^{2-}$

(JEE Advanced 2013)

- 7. Which of the following lanthanoid ions is diamagnetic? (Atomic numbers of Ce = 58, Sm = 62, Eu = 63, Yb = 70)
  - $(1) Eu^{2+}$

 $(2) \text{ Yb}^{2+}$ 

 $(3) \text{ Ce}^{2+}$ 

 $(4) \text{ Sm}^{2+}$ 

(JEE Advanced 2013)

- **8.** The color of KMnO<sub>4</sub> is due to:
  - (1)  $M \rightarrow L$  charge transfer transition
  - (2) d d transition
  - (3)  $L \rightarrow M$  charge transfer transition
  - (4)  $\sigma \sigma^*$  transition

(JEE Advanced 2015)

9. In the following reaction sequence in aqueous solution, the species X, Y and Z, respectively, are

$$S_2 O_3^{2-} \xrightarrow{Ag^+} X \xrightarrow[\text{Solution}]{\text{Clear solution}} \xrightarrow[\text{precipitate}]{\text{White}} Y \xrightarrow[\text{with time}]{\text{With time}} Y \xrightarrow[\text{Black precipitate}]{\text{Black precipitate}}$$

- (1)  $[Ag(S,O_3),]^{3-}$ ,  $Ag_2S,O_3$ ,  $Ag_2S$
- (2)  $[Ag(S_2O_3)_3]^{5-}$ ,  $Ag_2SO_3$ ,  $Ag_2S$
- $(3) [Ag(SO_3)_2]^{3-}, Ag_2S_2O_3, Ag$
- $(4) [Ag(SO_3)_3]^{3-}, Ag_5SO_4, AgS$

(JEE Advanced 2016)

- 10. Which of the following combination will produce H<sub>2</sub> gas?
  - (1) Fe metal and conc. HNO<sub>3</sub>
  - (2) Cu metal and conc. HNO<sub>3</sub>
  - (3) Zn metal and NaOH(aq)
  - (4) Au metal and NaCN (aq) in the presence of air

(JEE Advanced 2017)

### **Multiple Correct Answers Type**

- 1. Reduction of the metal centre in aqueous permanganate ion involves
  - (1) 3 electrons in neutral medium
  - (2) 5 electrons in neutral medium
  - (3) 3 electrons in alkaline medium
  - (4) 5 electrons in acidic medium

(IIT-JEE 2011)

- 2. The equilibrium 2 CuI  $\rightleftharpoons$  Cu + Cu<sup>II</sup> in aqueous medium at 25°C shifts towards the left in the presence of
  - (1) NO<sup>⊖</sup>

- (3) SCN<sup>⊖</sup>
- (2) Cl<sup>⊖</sup> (4) CN<sup>⊖</sup>

(IIT-JEE 2011)

- 3. Which one of the following arrangements does not represent the correct order of the property stated against it?
  - (1)  $Ni^{2+} < Co^{2+} < Fe^{2+} < Mn^{2+}$ : ionic size
  - (2)  $Co^{3+} < Fe^{3+} < Cr^{3+} < Sc^{3+}$ : stability in aqueous solution
  - (3) Sc < Ti < Cr < Mn: number of oxidation states
  - (4)  $V^{2+} < Cr^{2+} < Mn^{2+} < Fe^{2+}$ : paramagnetic behaviour

(JEE Advanced 2013)

- 4. The correct statement(s) about Cr<sup>2+</sup> and Mn<sup>3+</sup> is (are) [Atomic numbers of Cr = 24 and Mn = 25]
  - (1) Cr<sup>2+</sup> is a reducing agent
  - (2) Mn<sup>3+</sup> is an oxidizing agent
  - (3) Both  $Cr^{2+}$  and  $Mn^{3+}$  exhibit  $d^4$  electronic configuration
  - (4) When Cr<sup>2+</sup> is used as a reducing agent, the chromium ion attains  $d^5$  electronic configuration

(JEE Advanced 2015)

- 5.  $Fe^{3+}$  is reduced to  $Fe^{2+}$  by using
  - (1) H<sub>2</sub>O<sub>2</sub> in presence of NaOH
  - (2)  $Na_2O_2$  in water

- (3)  $H_2O_2$  in presence of  $H_2SO_4$
- (4) Na<sub>2</sub>O<sub>2</sub> in presence of H<sub>2</sub>SO<sub>4</sub>

(JEE Advanced 2015)

- 6. The correct statement(s) regarding the binary transition transition metal carbonyl compounds is (are) (Atomic number Fe = 26, Ni = 28)
  - (1) Total number of valence shell electrons at metal centre in Fe(CO)<sub>5</sub> or Ni(CO)<sub>4</sub> is 16
  - (2) These are predominantly low spin in nature
  - (3) Metal-carbon bond strengthens when the oxidation state of the metal is lowered
  - (4) The carbonyl C-O bond weakens when the oxidation (JEE Advanced 2018) state of the metal is increased

## **Linked Comprehension Type**

## Paragraph 1

p-Amino-N,N-dimethylaniline is added to a strongly acidic solution of X. The resulting solution is treated with a few drops of aqueous solution of Y to yield blue colouration due to the formation of methylene blue. Treatment of aqueous solution of y with reagent potassium hexacyanoferrate (II) leads to the formation of an intense blue precipitate. The precipitate dissolves on excess addition of the reagent. Similarly, the treatment of the solution of Y with the solution of potassium hexacyanoferrate(III) leads to a brown colouration due to the formation of Z.

- 1. Compound X is
  - (1) NaNO<sub>3</sub>
- (2) NaC1
- (3) Na<sub>2</sub>SO<sub>4</sub>
- (4) Na<sub>2</sub>S
- 2. Compound Y is
  - (1) MgCl<sub>2</sub>
- (2) FeCl<sub>2</sub>

(3) FeCl<sub>3</sub>

- (4) ZnCl<sub>2</sub>
- 3. Compound Z is
  - $(1) \text{ Mg}_2 [\text{Fe}(\text{CN})_6]$
- (2) Fe[Fe(CN)<sub>6</sub>]
- (3)  $Fe_4[Fe(CN)_6]_3$
- (4)  $K_2Zn_3[Fe(CN)_6]_2$

(IIT-JEE 2009)

## Paragraph 2

Copper is the most noble of the first row transition elements. It occurs in small deposits in several countries. Ores of copper include chalcanthite (CuSO<sub>4</sub>·5H<sub>2</sub>O), atacamite [Cu<sub>2</sub>Cl(OH)<sub>3</sub>], cuprite (Cu<sub>2</sub>O), copper glance (Cu<sub>2</sub>S), and malachite [Cu<sub>2</sub>(OH)<sub>2</sub>CO<sub>3</sub>] However, 80% of the world copper production comes from the ore chalcopyrite (CuFeS<sub>2</sub>). Extraction of copper from chalcopyrite includes roasting, iron removal; and self-reduction.

- 4. Partial roasting of chalcopyrite produces
  - (1) Cu<sub>2</sub>S and FeO
- (2) Cu<sub>2</sub>O and FeO
- (3) CuS and Fe<sub>2</sub>O<sub>3</sub>
- (4)  $Cu_2O$  and  $Fe_2O_3$
- 5. Iron is removed from chalcopyrite as
  - (1) FeO

(2) FeS

 $(3) \text{ Fe}_2O_3$ 

- (4) FeSiO<sub>3</sub>
- 6. In self-reduction, the reducing species is
  - (1) S $(3) S^{2-}$

- $(2) O^{2-}$
- (4) SO<sub>2</sub>
- (IIT-JEE 2010)

# <sub>paragraph</sub> 3

when a metal rod M is dipped into an aqueous colourless when address colourless concentrated solution of compound N, the solution turns light Addition of aqueous NaCl to the blue solution gives a white blue. Addition of aqueous NH<sub>3</sub> dissolves O and gives an intense blue solution.

- 7. The metal rod M is
  - (1) Fe

(2) Cu

(3) Ni

- (4) Co
- 8. The compound N is
  - (1) AgNO3
- $(2) Zn(NO_3)_2$
- (3) Al(NO<sub>3</sub>)<sub>3</sub>
- (4) Pb(NO<sub>2</sub>)<sub>2</sub>
- 9. The final solution contains
  - (1)  $[Pb(NH_3)_4]^{2+}$  and  $[CoCl_4]^{2-}$
  - (2)  $[Al(NH_3)_4]^{3+}$  and  $[Cu(NH_3)_4]^{2+}$
  - (3)  $[Ag(NH_3)_2]^{\oplus}$  and  $[Cu(NH_3)_4]^{2+}$
  - (4)  $[Ag(NH_3)_2]^{\oplus}$  and  $[Ni(NH_3)_6]^{2+}$

(IIT-JEE 2011)

## Matrix Match Type

1. Match the column.

Na	Column I ture of reaction/type	Column II Products	
a.	$O_2^{\ominus} \longrightarrow O_2 + O_2^{2-}$	p.	Redox reaction
b.	$\operatorname{CrO_4}^{2-} + \operatorname{H}^{\oplus} \longrightarrow$	q.	One of the products has trigonal planar structure
c.	$\frac{\mathrm{MnO}^{\Theta} + \mathrm{NO}_{2}^{\Theta} + \mathrm{H}^{\Theta}}{\longrightarrow}$	r.	Dimeric bridged tetrahedral metal ion
d.	$NO_3^{\Theta} + H_2SO_4 + Fe^{2+}$ $\longrightarrow$	s.	Disproportionation

(IIT-JEE 2007)

2. Match each of the reactions given in column I with the corresponding product(s) given in column II.

	Column I	13	Column II
a.	Cu + dil HNO <sub>3</sub>	p.	NO
b.	Cu + conc HNO <sub>3</sub>	q.	NO <sub>2</sub>
c.	Zn + dil HNO <sub>3</sub>	r.	N <sub>2</sub> O
d.	Zn + conc HNO <sub>3</sub>	s.	Cn(NO <sub>3</sub> ) <sub>2</sub>
		t.	$Zn(NO_3)_2$

(IIT-JEE 2009)

## **Numerical Value Type**

1. The oxidation number of Mn in the product of alkaline oxidative fusion of MnO2 is

(IIT-JEE 2009)

2. The number of water molecule(s) directly bonded to the metal centre in CuSO<sub>4</sub>·5H<sub>2</sub>O is

(IIT-JEE 2009)

3. Among the species given below, the total number of diamagnetic species is

H atom, NO<sub>2</sub> monomer, O<sub>2</sub> (superoxide), dimeric sulphur in vapour phase,

 $Mn_3O_4$ ,  $(NH_4)_2$  [FeCl<sub>4</sub>],  $(NH_4)_2$  [NiCl<sub>4</sub>],  $K_2MnO_4$ ,  $K_2CrO_4$ (JEE Advanced 2018)

4. To measure the quantity of MnCl<sub>2</sub> dissolved in an aqueous solution, it was completely to KMnO4 using the reaction,  $MnCl_2 + K_2S_2O_8 + H_2O \rightarrow KMnO_4 + HCl$  (equation not balanced). Few drops of concentraterd HCl ware added to this solution and gently warmed. Further, oxalic acid (225 mg) was added in protions till the colour of the permanganate ion disappeared. The quantity of MnCl, (in mg) present in the initial solution is \_

(Atomic weights in g mol<sup>-1</sup>: Mn = 55, Cl = 35.5) (JEE Advanced 2018)

# **Answers Key**

# **EXERCISES**

## Single Correct Answer Type

- **5.**(1) 4. (2) **3.** (3) 1.(3) **2.** (2) **10.** (1) 9. (2) **8.** (4) 6. (4) 7.(1) **15.** (2) **14.** (4) **13.** (2) 11. (4) **12.** (3) **20.** (2) **19.** (2) **18.** (4) **16.** (1) **17.** (2) 25. (4) **24.** (1) **23.** (3) 21. (4) **22.** (2) **30.** (2) **29.** (1) **26.** (1) **28.** (4) **27.** (2)
- **35.** (1) 34. (1) **33.** (3) 31. (3) **32.** (3) **40.** (2)
- **39.** (4) **38.** (1) 36.(1)**37.** (1) **45.** (3) **44.** (2) **43.** (4) 41. (3) **42.** (1)
- **50.** (2) 49. (4) **48.** (3) **47.** (2) **46.** (1) 54. (4) 55. (4) **53.** (1) **52.** (1) **51.**(1) **60.** (4) 59. (4) **58.** (1) **57.** (2) **56.** (3) **65.** (1) **64.** (3) **63.** (3) **62.** (3) **61.** (3) **70.** (3) **69.** (4) **68.** (2) **67.** (3) **66.** (1) **75.** (1) 74. (2) **73.** (4) 72.(1) **71.** (3) **80.** (2) **79.** (2) **78.** (2) **77.** (1) **76.** (2) **85.** (4) **84.** (4) **83.** (1) **82.** (2) **81.** (1) 90.(4) **99.** (3) **88.** (4) **87.** (2) **86.** (2) **95.** (2) 94. (2) **93**. (3) **92.** (4) **91**.(1) 99. (4) **100.** (2) **98.** (3) **97.** (1) **96.** (4)

101. (4)	<b>102.</b> (3)	<b>103.</b> (2)	<b>104.</b> (4)	<b>105.</b> (3)
106. (4)	<b>107.</b> (2)	<b>108.</b> (2)	<b>109.</b> (3)	<b>110.</b> (1)
<b>111.</b> (1)	<b>112.</b> (1)	<b>113.</b> (2)	<b>114.</b> (3)	<b>115.</b> (3)
<b>116.</b> (1)	<b>117.</b> (3)	<b>118.</b> (3)	119. (2)	<b>120.</b> (4)
<b>121.</b> (4)	<b>122.</b> (4)			

#### **Multiple Correct Answers Type**

<b>1.</b> (1, 2)	<b>2.</b> (3, 4)	<b>3.</b> (1, 2)
4. (2, 3)	<b>5.</b> (1, 3, 4)	<b>6.</b> (1, 3, 4)
7. (1, 4)	<b>8.</b> (1, 2, 4)	<b>9.</b> (1, 2)
10. (2, 3, 4)	11. (2, 3)	<b>12.</b> (1, 3)
<b>13.</b> (1, 2)	<b>14.</b> (1, 3, 4)	<b>15.</b> (2, 3)
<b>16.</b> (1, 2, 3)	<b>17.</b> (1, 2, 4)	<b>18.</b> (1, 2, 3)
	<b>20.</b> (1, 3)	<b>21.</b> (1, 2, 3)
<b>19.</b> (1, 2, 3)	<b>23.</b> (1, 2, 3)	<b>24.</b> (1, 2)
<b>22.</b> (2, 3, 4)	<b>26.</b> (1, 2, 4)	<b>27.</b> (2, 3)
<b>25.</b> (1, 2, 4)	<b>29.</b> (1, 2)	<b>30.</b> (1, 2, 3)
<b>28.</b> (1, 3, 4)		<b>33.</b> (2, 3, 4)
<b>31.</b> (2, 3)	<b>32.</b> (1, 2)	<b>36.</b> (3, 4)
<b>34.</b> (1,2,3)	<b>35.</b> (1, 2, 3)	<b>39.</b> (3, 4)
<b>37.</b> (2, 3, 4)	<b>38.</b> (1, 2, 3)	22- (2)
<b>40.</b> (2, 3, 4)		

# **Linked Comprehension Type**

1. (2) 6. (3) 11. (4) 16. (2) 21. (3) 26. (2) 31. (4)	2. (1) 7. (3) 12. (2) 17. (1) 22. (3) 27. (3)	3. (3) 8. (2) 13. (4) 18. (4) 23. (3) 28. (2)	4. (4) 9. (4) 14. (3) 19. (1) 24. (2) 29. (1)	5. (3) 10. (2) 15. (3) 20. (2) 25. (2) 30. (3)
31. (4)				

## Matrix Match Type

	T	h	c	d	e
Q. No.	a	D	t	р	_
1.	S	r	q, r	p, q	_
2.	p, q, r	r, s	- q, <i>r</i>	r	_
3.	q, s	q	P	p, s	_
4.	p, q, r	r	p, s	n	_
5.	q	S	r	Р	

q, r	р	S		
q	t	S	n	~
r	S	q		1
q	r	t	p	1
ii, iii→q	i, ii→p,q	iv→q,r	iv→s	8
ii, iii→p	i→s	iv→q		
	q r q ii, iii→q	$\begin{array}{c cc} q & t \\ \hline r & s \\ \hline q & r \\ \hline ii, iii \rightarrow q & i, ii \rightarrow p, q \end{array}$	$\begin{array}{c cccc} q & t & s \\ \hline r & s & q \\ \hline q & r & t \\ \hline ii, iii \rightarrow q & i, ii \rightarrow p, q & iv \rightarrow q, r \\ \end{array}$	$\begin{array}{c ccccc} q & t & s & p \\ \hline r & s & q & p \\ \hline q & r & t & p \\ \hline ii, iii \rightarrow q & i, ii \rightarrow p, q & iv \rightarrow q, r & iv \rightarrow s \end{array}$

## **Numerical Value Type**

1. (3)	<b>2.</b> (6)	<b>3.</b> (5)	<b>4.</b> (3)	5.(2)
<b>6.</b> (7)	<b>7.</b> (4)	<b>8.</b> (3)	<b>9.</b> (3)	10. (6)

#### **ARCHIVES**

JEE Advanced

#### **JEE Main**

## **Single Correct Answer Type**

_			4 (4)	_
	<b>2.</b> (2)	<b>3.</b> (1)	<b>4.</b> (4)	<b>5.</b> (4)
<b>1.</b> (3)	2. (2)	D. (1)		(,)

#### **7.** (3) **6.** (1)

## Single Correct Answer Type

Jing.				F (1)
4 (1)	<b>2.</b> (2)	<b>3.</b> (3)	<b>4.</b> (4)	<b>5.</b> (1)
<b>1.</b> (1)	2. (2)		0 (1)	<b>10.</b> (3)
6. (3)	<b>7.</b> (2)	<b>8.</b> (3)	<b>9.</b> (1)	10.(5)

## **Multiple Correct Answers Type**

6.(2,3)

# **Linked Comprehension Type**

		2 (2)	<b>4.</b> (1)	5. (4)
1. (4)	<b>2.</b> (3)	<b>3.</b> (2) <b>8.</b> (1)	<b>9.</b> (3)	
<b>6.</b> (3)	<b>7.</b> (2)	0. ( )		

## Matrix Match Type

1. 
$$(a \rightarrow p, s; b \rightarrow r; c \rightarrow p, q; d \rightarrow p)$$
  
2.  $(a \rightarrow p, s; b \rightarrow q, s; c \rightarrow r, t; d \rightarrow q, t)$ 

## **Numerical Value Type**

# Coordination Compounds

### **OVERVIEW**

- 1. Coordination compounds: Compounds in which the central atom is linked to a number of ions or neutral molecules called ligands by coordinate bonds i.e., by donation of lone pair of electrons by ligands to the central metal atom are called coordination compounds.
- 2. Double salts, mixed salts and complex compounds: Both double salts and complexes are formed by the combination of two or more stable compounds in stoichiometric ratio. Hence, they are additional molecular compounds.

However, double salts dissociate into simple substances or ions completely when dissolved in water, whereas in complex compounds, the complex ion almost does not dissociate. For example,

- a.  $KCl.MgCl_2 \cdot 6H_2O \longrightarrow K^{\oplus} + Mg^{2+} + 3Cl^{\Theta} + 6H_2O$ Carnallite (double salt)
- b. Bleaching powder  $CaOCl_2$  is a mixed salt. It is a salt of  $Ca^{2+}$  in which the anions present are  $Cl^{\Theta}$  and  $ClO^{\Theta}$ (hypochlorite ion). Similarly, NaKSO<sub>4</sub> is a mixed salt in which there are two cations Na<sup> $\oplus$ </sup> and K<sup> $\oplus$ </sup> ions and one anion SO.<sup>2-</sup>

one anion  $SO_4^{2-}$ .

c.  $K_4[Fe(CN)_6] \xrightarrow{} 4K^{\oplus} + [Fe(CN)_6]^{4-}$ Potassium ferrocyanide (Complex compound)

- 3. Ligands and central metal atom/ion: The donor atoms, molecules or anions which donate a pair of electrons to the metal atom or ion and form a coordinate bond with it are called **ligands**. The metal atom or ion to which these ligands are attached is called **central metal atom or ion**.
- 4. Denticity: The number of coordinating or ligating groups present in a ligands is called the denticity of that ligand.
- 5. Types of ligands: Ligands can be of the following types depending on the denticity of the ligand.
  - a. Monodentate or unidentate ligand: They have one donor atom, i.e. they donate only one lone pair of electrons to the central atom e.g., X<sup>⊖</sup>, H<sub>2</sub>Ö:, NH<sub>3</sub>,:CO, SCN<sup>⊖</sup> etc.
- b. Polydentate or multidentate ligands: These ligands coordinate using two or more donor atoms. Name and structures of some of them are shown below:

i. Bidentate ligands:  $\uparrow \qquad \uparrow$ Ethylenediamine(en)  $H_2 \ddot{N} (CH_2)_2 \ddot{N} H_2$  and

Oxalate ion  $(OX^{2-})$   $| COO^{\Theta} \rightarrow COO^{\Theta}$ 

ii. Tridentate or terdentate ligands:

Diethylenetriamine (diene):

iii. Tetradentate ligand:

Triethylene tetraamine (triene):

iv. Pentadentate ligand:

Tetraethylenepentaamine(tetraene):

v. Hexadentate ligand:

Ethylene diaminetetraacetato ion:

**6. Ambidentate ligands:** Unidentate ligands containing more than one coordinating atoms are called ambidentate ligands. e.g.,  $NO_2^{\ominus}$   $\left(O=N-O^{\ominus} \text{ and } O=N-O^{\ominus}: \rightarrow \right)$ .

e.g., 
$$NO_2^{\odot}$$
  $\left(\begin{array}{cc} O=N-O^{\odot} & \text{and } O=N-O^{\odot} \\ \downarrow & \\ & \left(\begin{array}{cc} \text{Nitrito-N} \end{array}\right) \end{array}\right)$  (Nitrito-O)

$$SCN^{\ominus}$$
  $\left(\begin{array}{c} \bigcirc \\ NCS: \longrightarrow \\ \text{(thiocyanato)} \end{array}\right)$  and  $\begin{array}{c} \bigcirc \\ SCN: \longrightarrow \\ \text{(isothiocyanato)} \end{array}$ 

7. Flexidentate ligands: Ligands which have more than one donor site, like SO<sub>4</sub><sup>2-</sup>, CO<sub>3</sub><sup>2-</sup> etc. such ligands can behave as monodentate ligand in one complex and bidentate in another complexes are known as flexidentate ligands.

EDTA generally acts as a hexadentate ligand but it can also act as a pentadentate and tetradentate ligand.

**8.** Coordination number (CN): It is defined as the number of coordinate bonds formed with the central atom/ion by the ligands, e.g.

$$[Cr(NH_3)_2Cl_2(H_2O)_2]^{\Theta}$$
,  $CN = 2 + 2 + 2 = 6$ 

Coordination number in case of polydentate ligands attached to central metal atom/ion is equal to number of polydentate ligand multiplied by their denticity, e.g.,

i. 
$$[Cr(en)_2(H_2O)_2]^{3+}$$
;  $CN = 2 \times 2 + 2 = 6$ 

ii. 
$$[Cr(edta)]^{\Theta}$$
;  $CN = 1 \times 6 = 6$ 

- 9. Coordination number (CN) of some central metal atom/ion. (Refer to Table 7.6).
- 10. Coordination sphere or coordination entity and counter ion: The central atom and the ligands which are directly attached to it are enclosed in square brackets and are collectively termed as coordination sphere or coordination entity.

The ionisable groups outside the square brackets are called counter ions, as shown in the compounds.

$$\begin{array}{c} [\text{Cr}(\text{NH}_3)_5\text{Cl}]\text{SO}_4 \longrightarrow [\text{Cr}(\text{NH}_3)_5\text{Cl}]^{2^+} + \text{SO}_4^{\ 2^-} \\ \text{Coordination compound} \\ & \swarrow \\ \text{Central metal } \\ & \downarrow \\ \text{Coordination sphere or entity} \\ \end{array}$$

- 11. Coordination polyhedron: The spatial arrangement of the ligand atoms which are directly attached to the central metal atom/ion in a definite direction thereby giving a definite geometry to the complex compound/ion is called coordination polyhedron around the central metal atom/ion. The various polyhedra are tetrahedral, square planar, octahedral, square pyramidal, trigonal bipyramidal, pentagonal bipyramidal etc.
- **12.** Oxidation number (ON) of central atom: It is defined as the charge that central metal ion would carry if all the ligands are removed along with electron pairs. For example, [CrBrCl(NH<sub>3</sub>)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>]ClO<sub>4</sub>] →

$$[\text{CrBr}^{^{1}}\text{Br}^{-1}\text{Cl}^{-1}(\text{NH}_{3}^{0})_{2}(\text{H}_{2}^{0}\text{O})_{2}]^{\oplus} + \text{ClO}_{4}^{\Theta}$$

Charge on complex ion = +1

Let charge on Cr = x

Total charge of ligands = -1 - 1 + 0 + 0 = -2

$$\therefore x-2=+1 \therefore x=3$$

Hence oxidation number of Cr = +3 or (III).

**Note:** The central atom in a complex compound /ion can be even a non-metal, e.g., in  $Ba[BrF_4]_2$ , central atom in complex ion is Br.

13. Chelation: When coordination of two or more donor atoms from a polydentate ligand to a single central atom/ion takes place forming a closed or cyclic ring structure, it is called chelation and the ligand is called a chelating ligand. The close ring compound thus formed is called chelate (or metal chelate). [Chelos, Greek word means 'crab']. For example, Tridentate chelation in [PtBr(dien)]

$$\begin{array}{c|c} CH_2 & CH_2 \\ & & H_2 \\ H_2 N: & : N \\ & & CH_2 \\ & & \vdots \\ & & CH_2 \\$$

Chelating ligands form more stable complexes that

- 14. Homoleptic, heteroleptic and labile complexes.

  Complex in which the metal atom/ion is linked to only one type of ligands are called homoleptic complexes, e.g., ion is linked to more than one kind of ligands are called heteroleptic complexes, e.g., [Cr(NH<sub>3</sub>)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>Br<sub>2</sub>]<sup>9</sup>. The complex in which ligand can easily be replaced by other ligands is called labile complex.
- 15. Homonuclear and polynuclear complexes: Complexes: in which only one metal atom is present are  $known_{1}$  as homonuclear complexes, e.g.,  $[Cr(H_2O)_6]^{3+}$ .  $Complexes_{in}$  which more than one metal atom/ion is present are known as polynuclear complexes, e.g.,  $[(en)_2CrCohCr(en)_2]$
- 16. Nomenclature and formula writing of coordination compounds: Refer to Section 7.5.
- 17. a. Werner's coordination theory: Refer to Section 7.6.
  - b. Werner's representation of complexes: For example in  $CoBr_3 \cdot xNH_3$ , the maximum value of  $x = CN \text{ of } C_0^{-1}$  which is equal to 6.

The minimum value of x = CN - O.S. = 3

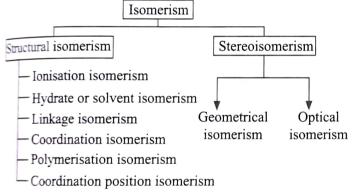
## Werner's coordination compounds

	Werner complex and colour	Modern notation	Ionisation	Primary valency satisfied by (ON)	Secondary valency satisfied by CN
(A)	CoCl <sub>3</sub> ·6NH <sub>3</sub> Yellow	[Co (NH <sub>3</sub> ) <sub>6</sub> ] Cl <sub>3</sub>	[Co (NH <sub>3</sub> ) <sub>6</sub> ] <sup>3+</sup> + 3Cl <sup>⊖</sup>	3Cl <sup>⊖</sup>	6NH <sub>3</sub>
(B)	CoCl <sub>3</sub> ·5NH <sub>3</sub> Purple	[CoCl (NH <sub>3</sub> ) <sub>5</sub> ] Cl <sub>2</sub>	[CoCl (NH <sub>3</sub> ) <sub>5</sub> ] <sup>2+</sup> + 2Cl <sup>©</sup>	3Cl <sup>⊙</sup> including one Cl <sup>⊙</sup> with both valencies)	5NH <sub>3</sub> one Cl <sup>Θ</sup>
(C)	CoCl <sub>3</sub> ·4NH <sub>3</sub> Exists in 2 isomers <i>cis</i> & <i>trans</i> with green and violet in colour	[CoCl <sub>2</sub> (NH <sub>3</sub> ) <sub>4</sub> ] Cl	[CoCl <sub>2</sub> (NH <sub>3</sub> ) <sub>4</sub> ] <sup>⊕</sup> + Cl <sup>⊖</sup>	3Cl <sup>⊕</sup> including 2Cl <sup>⊕</sup> with both valencies)	4NH <sub>3</sub> 2 Cl <sup>Θ</sup>
(D)	CoCl <sub>3</sub> ·3NH <sub>3</sub>	[CoCl <sub>3</sub> (NH <sub>3</sub> ) <sub>3</sub> ]	[CoCl <sub>3</sub> (NH <sub>3</sub> ) <sub>3</sub> ]	3Cl <sup>⊖</sup> all with both va- lencies or with dual	3NH <sub>3</sub> 3 Cl <sup>Θ</sup>

- c. Failure of Werner's coordiation theory: Refer to Section 7.6.2.
- 18. Sidgwick theory and effective atomic number (EAN):
  In order to explain the stability of complexes Sidgwick
  proposed EAN rule. He suggested that a metal ion will
  continue accepting electron pairs till the total number of
  electrons in the metal ion (after gaining one lone pair of
  electrons from the ligands) becomes equal to that of next
  higher noble gas. This total number of electrons is called
  EAN of the metal.

 $EAN = (Atomic number - OS) + (CN \times 2)$ For example,

- i. EAN in  $[Fe^{2+}(CN)_6]^{4-} = (26-2) + (6 \times 2) = 36$ = Z of Kr (36) (next nearest inert gas).
- ii. EAN in  $[\text{Fe}^{3+}(\text{CN})_6]^{3-} = (26-3) + (6 \times 2) = 35$   $\neq Z \text{ of Kr (36) (next nearest inert gas).}$ EAN rule is not valid in this case.
- 19. Isomerism: Isomers are compounds having same molecular formula but different structures. The following types isomerism are:



#### 20. Structural isomerism:

- i. Ionisation isomerism: This type of isomerism exists
  when a counter ion in a coordination compound is itself
  a potential ligand. For example,
  - **a.**  $[Cr(NO_3)(NH_3)_5]SO_4$  and  $[Cr(SO_4)(NH_3)_5](NO_3)$
  - **b.**  $[\overset{+3}{\text{CoCl}}_2^2(N\overset{0}{\text{H}}_3)_4]\text{Br}_2$  and  $[\overset{+3}{\text{CoBrCl}}(N\overset{-1}{\text{H}}_3)_4]\text{Cl}$
- ii. Hydrate or solvent isomerism: It occurs when water forms a part of the coordination entity or is outside it. For example, CrCl<sub>3</sub>·6H<sub>2</sub>O exists in
  - a. [Cr(H<sub>2</sub>O)<sub>6</sub>]Cl<sub>3</sub> (violet) gives 4 ions in solution.
  - **b.**  $[CrCl(H_2O)_5]Cl_2 \cdot H_2O$  (pale green) gives 3 ions in solution.
  - **c.** [CrCl<sub>2</sub>(H<sub>2</sub>O)<sub>4</sub>]Cl·2H<sub>2</sub>O (dark green) gives 2 ions in solution
  - **d.** [CrCl<sub>3</sub>(H<sub>2</sub>O)<sub>3</sub>]·3H<sub>2</sub>O gives no ions in solution.
- iii. Linkage isomerism: This type of isomerism is possible in any coordination compounds containing an ambidentate ligand like NO<sub>2</sub><sup>⊙</sup>, or SCN<sup>⊙</sup> or CN<sup>⊙</sup>. This type of isomersim arises due to different metal-ligand (M ← L) linkage. For example, [Co(NH<sub>3</sub>)<sub>5</sub>NO<sub>2</sub>]<sup>2+</sup>

has two isomeric forms having red and yellow colours. The red colour isomer is  $[Co(NH_3)_5(ONO)]^{2+}$  (having  $Co \leftarrow O$  linkage) while the yellow isomer is  $[Co(NH_3)_5(NO_2)]^{2+}$  (having  $Co \leftarrow N$  linkage).

iv. Coordination isomerism: Coordination compounds made up of cationic and anionic coordination entities, show this type of isomerism due to interchange of ligands between the cation and anion entities. For example,

 $[Cr(NH_3)_6]$   $[Co(CN)_6]$  and  $[Co(NH_3)_6]$   $[Cr(CN)_6]$ 

v. Polymerisation isomerism: This type of isomerism exists among complexes which have same empirical formula but each of the isomer is some multiple of the empirical formula, e.g.

$$\begin{split} & [\text{Pt}(\text{NH}_3)_2\text{Cl}_2], [\text{Pt}(\text{NH}_3)_4] [\text{Pt}\text{Cl}_4] \text{ and} \\ & [\text{Pt}(\text{NH}_3)_3\text{Cl}]_2 [\text{Pt}\text{Cl}_4] \end{split}$$

These isomers are distinguished by mass spectroscopic methods.

vi. Coordination position isomerism: This type of isomerism is shown in polynuclear complexes due to interchange of ligands between the coordination spheres of various central metal ion, e.g.,

$$[(NH_3)_4Cr < NH_2 > Cr(NH_3)_2Br_2]^{2^+}$$
 and  $[Br(NH_3)_3Cr < NH_2 > Cr(NH_3)_3Br]^{2^+}$ 

- vii. Stereoisomerism: This type of isomerism is due to differences in arrangement of ligands in space around a given metal atom/ion. It is of the following two types:
- A. Geometrical isomers (GI):

**cis—trans isomerism:** This type of isomerism occurs in complexes having coordination number (CN) 4 (square planar) and 6 (octahedral) complexes.

- a. Complexes with general formula Ma<sub>4</sub>, Mab<sub>3</sub> and Ma<sub>3</sub>b (square planar geometry with CN = 4) and Ma<sub>6</sub> and Ma<sub>5</sub>b or Mab<sub>5</sub> (octahedral geometry with CN = 6) do not show GI.
- **b.** Complexes with general formula Ma<sub>2</sub>b<sub>2</sub> (where both 'a' and 'b' are monodentate) shows 2 isomers (*cis* and *trans*), e.g., [Pt(NH<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>]
- c. Ma<sub>2</sub>bc type shows 2 iosmers (cis and trans),
   e.g., [Pt(NH<sub>3</sub>)<sub>2</sub>ClBr]
- **d.** Mabcd type shows 3 geometrical isomers, e.g., [Pt(NH<sub>3</sub>)Cl Br I]
- e. Square planar complexes having unsymmetrical bidentate ligands, show 2 GI (*cis* and *trans*) e.g., [Pt(Gly)<sub>2</sub>].
- f. Octahedral complexes of type Ma<sub>4</sub>b<sub>2</sub> and Ma<sub>3</sub>b<sub>3</sub> each exhibit 2 G.I. respectively. In case of Ma<sub>4</sub>b<sub>2</sub> it is classified as *cis* and *trans* and in case of Ma<sub>3</sub>b<sub>3</sub>, it is classified as facial (fac-) and meridional (mer-).
- g. Octahedral complexes of type Mabcdef can have 1/5 geometrical isomers.

h. Geometrical isomers do not occur in tetrahedral complexes (CN = 4) because the relative position of the ligands attached to the central metal atom/ion is same w.r.t. each other.

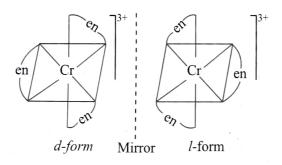
#### B. Optical isomerism:

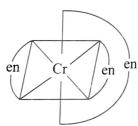
- a. The coordination compounds having same molecular formula but differing in their ability to rotate directions of the plane of polarised light are said to exhibit optical isomerism and such molecules are called optical isomers (enantiomers or enantiomorphs).
- **b.** General formulae of optically active complexes
  - i.  $[M(AA)_3]^{n\pm}$ ,  $[M(AA)_2a_2]^{n\pm}$ ,  $[M(AA)_2ab]^{n\pm}$ ,  $[M(AA)a_2b_2]^{n\pm}$ , (where AA are symmetrical bidentate ligands)
  - ii.  $[Ma_2b_2c_2]^{n\pm}$ ,  $[Mabcdef]^{n\pm}$ ,  $[M(AB)_3]^{n\pm}$

#### C. Some examples:

i.  $[M(AA)_3]^{n\pm}$ , e.g.,  $[Cr(en)_3]^{3+}$  (3 stereoisomers)

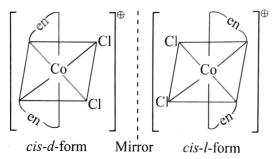
(where AB are unsymmetrical ligands)





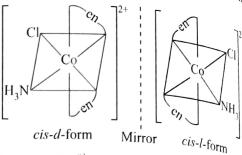
'Meso' or optically inactive form (if exists)

ii.  $[M(AA)_2a_2]^{n\pm}$ , e.g.,  $[Co(en)_2Cl_2]^{\oplus}$ cis form = 3, (each showing optical isomerism) trans form = 1 (does not show optical isomerism)



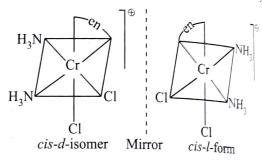
iii.  $[M(AA)_2ab]^{n\pm}$ , e.g.,  $[Co(en)_2(NH_3)C1]^{2+}$ (3 stereoisomers) (one *cis* and one *trans*)

cis form is optically active but the trans form  $f_{0}$ 

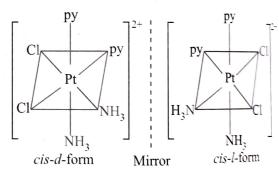


iv.  $[M(AA)a_2b_2]^{n\pm}$ , e.g.,  $[CrCl_2(en)(NH_3)_2]^{\oplus}$  (one *cis* and one *trans*)

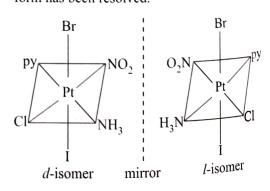
cis form is optically active but *trans* form is optically inactive.



v.  $[Ma_2b_2c_2]^{n\pm}$ , e.g.,  $[Pt(py)_2(NH_3)_2Cl_2]^{2+}$ (one *cis* and one *trans*) *cis* form is optically active but *trans* form is optically inactive.

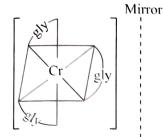


vi. [Mabcdef]<sup>n±</sup>, e.g., [Pt(py)NH<sub>3</sub>NO<sub>2</sub>ClBrI] shows 15 geometrical isomers. Each of them is optically active. Only 3 isomers have been prepared but no form has been resolved.



vii. [M(AB)<sub>3</sub>], e.g., [Cr(gly)<sub>3</sub>]
2 cis and 2 trans forms.

Both the forms are optically active.



gly Cr

cis or trans-d-isomer

cis or trans-l-isomer

- viii. Both  $[Ma_4b_2]^{n\pm}$  and  $[Ma_3b_3]^{n\pm}$  types show two geometrical isomers (*cis* and *trans*) or fac- and mer-). But none of them are optically active.
- ix. Octahedral complexes containing hexadentate ligands e.g.. [Cr(edta)]<sup>⊙</sup> show optical isomerism, i.e., d- and l-form.
- 11. **Bonding in coordination compounds:** To explain the definite geometry, magnetic and optical properties of coordination compounds, various theories were put forward, e.g..
  - i. Valence bond theory (VBT) in 1930s
  - ii. Crystal field theory (CFT) in 1950s and 1960s
  - iii. Ligand field theory (LFT) in 1960s onwards
  - iv. Molecular orbital theory (MOT) in 1960s onwards But only first two theories are discussed in this chapter.
- 22. a. Valence bond theory (VBT): Refer to Section 7.10
  - b. Drawbacks of VBT: (Refer to Section 7.10.6)
  - c. Refer to Table 7.17, for geometry (shape), hybridisation and magnetic properties of some of the complexes.
- 23. Crystal field theory (CFT): (Refer to Section 7.11)

#### 24. Spectrochemical Series:

Some ligands have been arranged below from the weakest to the strongest. This arrangement is called spectrochemical series as shown below:

$$\underline{I^{\ominus} < Br^{\ominus} < S^{2-} < SCN^{\ominus} < CI^{\ominus} < F^{\ominus} < NO_{3}}^{\ominus} < \overset{\Theta}{O}H < urea < EtOH$$

Weak field ligand

$$\leq C_2O_4^{2-}(OX) \leq O^{2-} \leq H_2O \leq NCS^{\Theta} \leq EDTA \leq NH_3$$

Border line field ligands

 $\le$  NH<sub>3</sub>, pyridine  $\le$  ethylenediammine (en)  $\le$  dipyridyl (dipy)  $\le$  phen  $\le$  NO<sub>2</sub>  $\le$  CN  $\le$  CO

Strong field ligands

A pattern of increasing  $\sigma$  donation is:

# $Halide\ donors \leq N\ donors \leq C\ donors$

Note: Oxalate, generally behaves as weak field ligand but with  $C_0$  (cobalt), it behaves as a strong field ligand like  $NH_3$  e.g.; in the compound  $[Co(OX)_3]^{3-}$ .

# 25. Limitation of CFT:

a. Assuming ligands as point charges, it follows that anionic ligands should exert greatest splitting effect, but anionic ligands are found at low end of the spectrochemical series.

- **b.**  $OH^{\odot}$  lies below  $H_2O$  and  $NH_3$  in spectrochemical series, but it produces a greater splitting.
  - These above weakness of CFT are explained by LFT (Ligand field theory)
- 26. Stability of coordination compounds: (Refer to Section 7.14)
- 27. Organometallic compound (OMC): They contain at least one M–C bond. [Ni(CO)<sub>4</sub>] is taken as OMC although CO is not organic compound. Metal cyanides (e.g. KCN) are not included in OMC, although they contain M–C bond.

#### A. OMC are of two types:

- i. s- and p-block OMC or  $\sigma$  complexes
- ii. d- and f-block OMC or  $\pi$ -complexes.
- **s- and p-block OMC:** The bonds in alkyls of s-block elements are highly polar.

In the OMC of group 14, 15 and 16, M–C bonds are of relative lower polarity.

Methyl compounds of Li, Na, Be, Mg and Al are associated with alkyl bridges and multicentre 2 electron bond. e.g., Li<sub>4</sub>(CH<sub>3</sub>)<sub>4</sub>, Al<sub>2</sub>(CH<sub>3</sub>)<sub>6</sub>.

- B. d- and f-block O.M.C.
  - i. Zeise's salt:  $[PtCl_3(C_2H_4)]^{\Theta}$  or  $K[PtCl_3(\eta^2-C_2H_4)]$
  - ii.  $[Ni(CO)_4]$ ,  $[Cr(CO)_6]$ ,  $Co_2(CO)_8$ ,  $[Fe_2(CO)_9]$ .  $[Mn_2(CO)_{10}]$ ,  $Fe(CO)_5$ ,  $Fe_3(CO)_{12}$ .
  - iii. Ferrocene:

[Fe( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>] (bicyclopentadienyl iron(II)) and dibenzene chromium [Cr( $\eta^6$ -C<sub>5</sub>H<sub>6</sub>)<sub>2</sub>]

These compounds are called METALLOCENE or sandwich compounds which have  $\pi$ -bonding of carbocyclic rings to metal atoms.

They are highly specific for homogeneous catalysis process like carbonylation, hydrogenation and polymerisation.

**28. a. Metal carbonyls:** Homoleptic carbonyls (compounds containing CO ligands only) formed by most of TE.

Metal carbonyls are not regarded as organometallic compounds (OMC) in the true sense because CO is not an organic compound. However, they are studied along with other OMCs.

b. Nature of bonding in metal varbonyls: CO, as a ligand binds to CMA by C-atom forming weak σ-bond to the CMA, CO acts also as an acceptor ligand and forms a π-bond to the metal. This is called synergic bonding which stabilises the (M←L) interaction.

#### 29. Importance of coordination compounds:

- a. *cis*-platin and taxol are used in cancer (tumours) therapy.
- **b.** Coordination compounds are of great importance to biological system e.g.
  - i. Chlorophylls (the green plant pigment that acts as a photosensitiser in the photosynthesis in plants Ligand = Porphyrin, CMA = Mg<sup>2+</sup>)
  - ii. Haemoglobin (acts as O<sub>2</sub> carrier, red pigment of blood) [Ligand =Porphyrin, CMA = Fe<sup>2+</sup>]

- iii. Myoglobin (which stores  $O_2$  and is a regulator of respiration. (Ligand = Porphyrin, CMA =  $Fe^{2+}$ )
- iv. Vitamin  $B_{12}$  or cyanocobalamine (antipernicious anaemia factor. Ligand = Corrin, CMA =  $Co^{2+}$ )
- v. Enzyme e.g., carboxy peptidase A and carbonic anhydrase (catalysis of biological system, CMA =  $Zn^{2+}$ )
- c. Extraction of Au and Ag: The noble metals like Au and Ag are extracted from their ores through the formation of cyanide complexes e.g.  $[Au(CN)_2]^{\Theta}$  in aqueous solution and Au is precipitated by addition of Zn metal.
- **d. Purification of metals (Mond's process):** Impure Nickel is converted to [Ni(CO)<sub>4</sub>] which on decomposition gives pure Ni.
- e. When certain metals are present in toxic proportions in plant and animal system, they are removed by chelating ligand, e.g., excess of Cu and Fe is removed by the chelating ligands. D-Pencillamine and desferrioxime B via the formation of coordination compounds.
- **f.** Calcium dihydrogen salt of EDTA is used in treatment as an antidote for the Pb poisoning.
- g. EDTA is used in determining the hardness of  $H_2O$ .  $Ca^{2+}$  and  $Mg^{2+}$  can be selectively estimated because of difference in their  $K_a$  values.  $K_a$  value of  $Mg^{2+}$  complex  $> K_a$  value of  $Ca^{+2}$  complex.
- **h.** Ziegler–Natta [TiCl<sub>4</sub> + (C<sub>2</sub>H<sub>5</sub>)<sub>3</sub>Al], a heterogenous catalyst (insoluble in the reaction medium) is used in the polymerisation of alkenes at atmospheric pressure and at ambient temperature (i.e., for the preparation of HDPE).
- i. Wilkinson's homogeneous catalyst [RhCl(PPh<sub>3</sub>)<sub>3</sub>] (soluble in the reaction medium) is used in the hydrogenation of alkene.

j. Many ligands (organic reagents) are used for the gravimetric estimation of number of metal ions

S. No.	Metal ion to be estimated	Colour	рH	Organic Reagent
1.	Cu <sup>2+</sup>	Red	pH = 9-10	Benzoin ovin
2.	Ni <sup>2+</sup>	Red	pH = 9–10	DMG
3.	Fe <sup>3+</sup>	Brown	_	1, 10-phenth- roline (ph)
4	A1 <sup>3+</sup>	Blue		8-hydroxy- quinoline
5.	Co <sup>2+</sup>	Red	-	α-nitroso- β- naphthol

k. Test for S<sup>2-</sup> ion: The complex sodium nitroprusside, Na<sub>2</sub>[Fe<sup>II</sup>(CN)<sub>5</sub>NO<sup>⊕</sup>] with S<sup>2-</sup> gives violet colour.

$$S^{2-} + [Fe^{II}(CN)_5NO^{\oplus}]^{2-} \longrightarrow [Fe^{II}(CN)_5(NOS)^{\ominus}]^{\perp}$$
Sulphide ion Violet colour

**l. Badecker reaction:** This reaction is used for test of sulphite ion.

$$Na_{2}[Fe^{II}(CN)_{5}NO^{\oplus}] + Na_{2}SO_{3} \longrightarrow Na_{4}[Fe(CN)_{5}(NOSO_{5})]$$
  
Sod. nitroprusside Sod. sulphite

- **m.** Everitt's salt: It is K<sub>2</sub>[Fe(CN)<sub>6</sub>], obtained by reduction of Prussian blue.
- **n.**  $[Fe^{II}(CN)_6]^{4-}$ ,  $[Fe^{III}(CN)_6]^{3-}$  and  $SCN^{\Theta}$  ions are used for the detection of various metal ions as shown below:

S. No.		Fe <sup>2+</sup>	Fe <sup>3+</sup>	Zn <sup>2+</sup>	Cu <sup>2+</sup>	Co <sup>2+</sup>
	[Fe <sup>II</sup> (CN) <sub>6</sub> ] <sup>4</sup> - Ferrocyanide ion	Ferro-ferrocyanide	Fe <sub>4</sub> <sup>III</sup> [Fe <sup>II</sup> (CN) <sub>6</sub> ] <sub>3</sub> Ferri-ferrocyanide (Prussian blue)	Zn <sub>2</sub> [Fe <sup>III</sup> (CN) <sub>6</sub> ] Bluish white ppt.	Cu <sub>2</sub> [Fe <sup>II</sup> (CN) <sub>6</sub> ] Chocolate ppt.	-
2.	[Fe <sup>III</sup> (CN) <sub>6</sub> ] <sup>3-</sup> Ferricyanide ion	$\operatorname{Fe_3^{II}[Fe^{III}(CN)_6]_2}$	Fe <sup>III</sup> [Fe <sup>III</sup> (CN) <sub>6</sub> ] Ferri-ferricyanide (Brown solution)	_	_	Co <sub>3</sub> <sup>II</sup> [Fe(CN) <sub>b</sub> ] Reddish brown colour
3.	SCN <sup>⊖</sup> Thiocyanate ion	<del>-</del> .	[Fe <sup>III</sup> (SCN) <sub>3</sub> ] Blood red colour	-	_	[Co <sup>ll</sup> (SCN) <sub>4</sub> ] <sup>2</sup> - Blue colour

# 1.1 INTRODUCTION

transition elements form a large number of complex The member of complex such are bound to a number of neutral molecules such are fanions or neutral molecules, such compounds are called of amounts are called configuration compounds. Chlorophyll, haemoglobin and vitamin are coordination compounds of Mg, Fe and Co respectively. be and correspectively.

If the corresponding the processes, industrial catalysis and Variety and reagents involve the use of coordination compounds. these compounds also find many applications, e.g. electroplating, extile dyeing and medicinal chemistry.

# 7.2 COMPLEX ION

it is defined as an electrically charged ion which consists of entral metal atom/ion linked to group of molecule ions by means of coordinate bonds.

In general, complex ion is represented as  $[ML_n]^{\pm x}$  where M is entral metal ion, L is ligand bonded to M by means of coordinate hand n is the coordination number of metal M and x is the net tharge on the complex.

The main points of difference between a double salt and a complex compound are summarised in Table 7.1.

Table 7.1 Difference between a double salt and a complex compound

S. No.	Double salt	S. No.	Complex compound
1.	They exist only in the solid state. In aqueous solution, they dissociate completely into ions.	1.	They exist in solid state as well as in aqueous solution, because the complex ion does not dissociate into ions.
2.	They usually contain two simple salts in equimolar propor- tions.	2.	The simple salts from which they are formed may or may not be in equimolar proportions.
3.	They are ionic compounds and do not contain any coordinate bond.	3.	They may or may not be ionic but the complex part always contains coordinate bonds.
4.	The metal ions show their normal valency.	4.	The metal ion satisfies its two types of valencies called primary and secondary valencies (discussed in Section 7.5).
5.	They lose their identity in the solution.	5.	They retain their identity in the solution.
6.	The properties of double salts are same as those of their constituent compounds.	6.	The properties of these compounds are different from its constituents.

Note: Compounds like K<sub>3</sub>[Co(NH<sub>3</sub>]<sub>6</sub>, K<sub>4</sub>[Fe(CN)<sub>6</sub>] etc. in which the complex ion is quite stable and almost does not dissociate into ions in the solution are called 'perfect complexes' or 'penetrating <sup>complexes</sup>. Compounds like K<sub>2</sub>[Cd(CN)<sub>4</sub>], in which the complex ion is not very stable and dissociates to greater extent to give simple ions are called 'imperfect or normal complexes'.

#### 7.2.1 Types of Complex

- 1. Cationic complex or positively charged complex: Complex ion  $[Cu(NH_3)_4]^{2+}$  in  $[Cu(NH_3)_4]SO_4$ , on ionisation gives  $[Cu(NH_3)_4]^{2+}$  and  $SO_4^{-2-}$  ions.  $[Cu(NH_3)_4]SO_4$  carries net positive charge.
- 2. Anionic complex or negatively charged complex: Complex  $K_3[Fe(CN)_6]$  gives three  $K^{\oplus}$  and  $[Fe(CN)_6]^{3-}$  ions on ionisation. Complex ion  $[Fe(CN)_6]^{3-}$  in  $K_3[Fe(CN)_6]$  carries net negative charge.
- 3. Neutral complex has cation and anion both as complex ion:  $Complex~[Pt(NH_3)_4]~[PtCl_4]~has~[Pt(NH_3)_4]^{2+}~and~[PtCl_4]^{2-}$ as cationic and anionic complex ion.
- 4. Neutral complex having no net charge, e.g. [Ni(CO)<sub>4</sub>].

# 7.3 SOME IMPORTANT TERMS USED IN COORDINATION COMPOUND

#### 7.3.1 COORDINATION ENTITY AND COUNTER ION

A coordination entity constitutes a central atom/ion (usually a metal) to which are attached a fixed number of molecules/ ions. It may be neutral or charged. This is also known as coordination sphere and is written inside [] brackets, e.g. [Ag(CN)<sub>2</sub>]<sup> $\Theta$ </sup> The ions present outside the coordination sphere constitute the counter ion/ionisation sphere.

The coordination entity and counter ions in the following coordination compounds:

 $[Cr(NH_3)_6]Cl_3$ ,  $K_4[Fe(CN)_6]$ ,  $K_2[PtCl_4]$ ,  $[Ni(CO)_4]$ ,  $K_2[Ni(CN)_4]$ ,  $O_2[PtF_6]$ ,  $Xe[PtF_6]$  are as shown below.

Coordination compound	Coordination entity	Type of coordination entity	Counter
[Cr(NH <sub>3</sub> ) <sub>6</sub> ]Cl <sub>3</sub>	[Cr(NH <sub>3</sub> ) <sub>6</sub> ] <sup>3+</sup>	Positively charged or cationic	3Cl <sup>©</sup>
K <sub>4</sub> [Fe(CN) <sub>6</sub> ]	$[Fe(CN)_6]^{3-}$	Anionic	4K <sup>⊕</sup>
K <sub>2</sub> [PtCl <sub>4</sub> ]	$[PtCl_4]^{2-}$	Anionic	2K <sup>⊕</sup>
Ni(CO) <sub>4</sub> ]	[Ni(CO) <sub>4</sub> ]	Neutral	
K <sub>2</sub> [Ni(CN) <sub>4</sub> ]	$[Ni(CN)_4]^{2-}$	Anionic	2K <sup>⊕</sup>
$O_2[PtF_6]$	$[Pt^{+5}F_6]^{\Theta}$	Anionic	$O_2^{\oplus}$ (Dioxygenyl)
Xe[PtF <sub>6</sub> ]	$[Pt^{+5}F_6]^{\Theta}$	Anionic	Xe <sup>⊕</sup>

## 7.3.2 CENTRAL ATOM/ION

In the coordination entity, the atom/ion (usually a metal) to which one or more neutral or charged molecules are bound by means of coordinate bond formation in a definite geometrical arrangement around it, is called the central atom/ion.

The central atom/ion is also known as centre of coordination, e.g., the central atom/ion in the following compounds  $[Co(NH_3)_6]$  $Cl_3$ ,  $K_3$ [Fe(CN)<sub>6</sub>], [PtCl<sub>4</sub>(NH<sub>4</sub>)<sub>2</sub>], [Ni(CO)<sub>4</sub>] are as shown below.

Complex	Central ion
[Co(NH <sub>3</sub> ) <sub>6</sub> ]Cl <sub>3</sub>	Co <sup>3+</sup>
K <sub>3</sub> [Fe(CN) <sub>6</sub> ]	Fe <sup>3+</sup>
[PtCl <sub>4</sub> (NH <sub>3</sub> ) <sub>2</sub> ]	Pt <sup>4+</sup>
[Ni(CO) <sub>4</sub> ]	Ni <sup>0</sup>

#### 7.3.3 LIGANDS

Any molecule/ion which can donate at least a pair of electron to the central atom/ion to form a coordinate bond is known as ligand or coordinating group. Further in a ligand, the atom which actually donates the pair of electron is called as donor atom or ligating atom.

Complex formation can be explained in terms of Lewis acid—Lewis base concept. Central atom/ion which accepts electron pair(s) from ligands act as Lewis acid, whereas ligands which donate one or more pair of electron to central atom/ion acts as Lewis base. This also explains why transition elements having empty *d*-orbitals form coordination compounds easily.

#### 7.3.3.1 Classification of Ligands

Ligands can be classified on the basis of denticity, i.e. the number of donor atoms present in the ligand molecule, which are forming coordinate bond with the central atom/ion, as follows:

a. Monodentate or unidentate ligands: If the ligand coordinates with central atom/ion using only one donor atom (irrespective of the number of donor atoms in it), it is known as monodentate ligand. These ligands may be neutral molecules or ionic. Examples of monodentate ligands are

Table 7.2 Some examples of monodentate or unidentate ligands

Neutral ligands		Negat ligan		Positive ligands	
←:NH <sub>3</sub>	Am- mine	I		NO⊕	Nitroso.
H₂Ö: →	Aqua	Cl <sup>⊖</sup>	Chlo- rido	H <sub>2</sub> N−NH <sub>3</sub>	nium Hyra- zinium
←:PH <sub>3</sub>	Phos- phine	O CH <sub>3</sub> −C−O	Ac- etato		Simum
<b>←:</b> CO	Car- bonyl	N <sup>3-</sup>	Ni- trido		
←:NO	Nitro- syl	NH <sub>2</sub> ⊖	Ami- do		

b. Polydentate or multidentate ligands: When two or more donor atoms present in the ligand coordinates with the central ion, the ligand is known as polydentate ligand. These may be bidentate, tridentate, tetradentate, pentadentate, hexadentate when it is coordinated with the central atom ion at 2, 3, 4, 5, 6 sites respectively. In other words, one molecule/ion of these ligands makes 2, 3, 4, 5, 6 (M \( \infty \) L) coordinate bonds respectively. Examples of polydentate ligands are given in Table 7.3.

Table 7.3 Some examples of polydentate ligands

Rido	entate or didentate ligand		Charge	Donor atoms	IUPAC Name	
i.	Ethylenediamine(en)	$\uparrow \qquad \uparrow \qquad \uparrow \qquad \qquad \uparrow \qquad \qquad \\ \text{H}_2 \ddot{\text{N}} - \text{CH}_2 - \text{CH}_2 - \ddot{\text{N}} \text{H}_2$	zero	Two N-atoms	1,2-Ethanediamine	
ii.	2, 2-Dipyridyl (dipy)	O O O	zero	Two N-atoms	Dipyridyl	
iii.	Oxalate ion	0 C − 0 C − 0 C − 0 Si:	-2	Two O-atoms	Oxalato	
iv.	Glycinate ion	$H_2C$ $C$ $C$ $C$ $C$ $C$ $C$ $C$ $C$ $C$	-1	N, O	Glycinato	
v.	Ortho-phenanthroline (Phen) or (ph)		zero	Two N-atoms	1, 10-Phenanthroli	
vi.	Carbonate ion	O=C Ö:0	-2	Two O-atoms	Carbonato	

Tridentate or terde	ntate ligand:					
i. Diethylene	triamine (dien)		zer	o Three N-	atoms	[N-(2-amminoethyl)- 1, 2-ethanediamine]
ii. 2, 2-2, Ter	pyridene (terpy)		zer	o Three N	-atom	Terpyridine
Tetradentate ligand	:					
Triethylene tetramine (trien)	1	$\uparrow$	zero	Four N-atoms	-	-bis-(2-aminoethyl)-1, nediamine]
<sub>pentadentate</sub> ligano	l:				,	
Ethylenediamine triacetate ion		$\begin{array}{c} \uparrow \\ -\mathrm{CH_2-CH_2N} \\ \leftarrow \\ \mathrm{CH_2CO} \\ \end{array} \\ \begin{array}{c} \uparrow \\ \mathrm{CH_2CO} \\ \end{array} \\ \begin{array}{c} \ominus \\ \rightarrow \end{array} \\ \end{array}$	-3	Two N and three O-atom	18 37 V	nediaminetriacetato
Hexadentate ligand	THE RESERVE OF THE RESERVE OF THE PARTY OF T	2				
Ethylenediamine tetraacetate ion (edta <sup>4</sup> )		$\begin{array}{c} \uparrow \\ -\text{CH}_2\text{-CH}_2\text{-N} \\ \text{CH}_2\text{CO} \\ \end{array}  \begin{array}{c} \uparrow \\ \text{CH}_2\text{CO} \\ \end{array}  \begin{array}{c} \uparrow \\ \rightarrow \end{array}$	-4	Two N and four O-atom		mediaminetetraacetato

Note: Polydentate ligands have flexible character. In simple terms, it is not necessary that all the donor atoms present in the polydentate ligand should form coordinate bond with central atom/ion. For example, ethylenediaminetetraacetic acid (EDTA) which is hexadentate ligand can also function as pentadentate or tetradentate ligand with certain metal ions.

c. Ambidentate ligands: Certain ligands have two or more donor atoms in their structure but while forming a complex only one donor atom/ligating site coordinates to the central atom/ion. Such ligands are known as ambidentate ligands, e.g.  $SCN^{\ominus}$ ,  $NO_2^{\ominus}$  ion etc. When the ambidentate ligand having two different donor atoms coordinate to the central atom/ion through either of its donor atoms, two different complexes are formed. These complexes are different because they have different structures. Such coordination compounds are called linkage isomers and the phenomenon is called linkage isomerism.

Examples of certain ambidentate ligands are given in Table 7.4.

Table 7.4 List of certain ambidentate ligands

Ambidentate ligand		Donor atom Name		Linkage	
a,	NO <sub>2</sub> <sup>©</sup>	N	nitrito or nitrito-N	$M \leftarrow NO_2^{\Theta}$	
	1102	O	isonitrito or nitrito-O	M←:ONO <sup>⊖</sup>	
b.	CN <sup>⊖</sup>	С	cyano or cyano-C	M←:CN <sup>⊖</sup>	
	CN	N	isocyano or cyano-N	M←:NC <sup>⊖</sup>	
c.	SCN <sup>⊖</sup>	S	thiocyanato or thiocyanato-S	M←:SCN <sup>⊖</sup>	
	SCN	N	isothiocyanato or thiocyanato-N	M←:NCS <sup>Θ</sup>	

**d. Bridging ligand:** Certain ligands e.g.  $N_2$  or :N $\equiv$ N:,  $N_2 - N_1 = N_2$ ,  $N_2 - N_2 = N_2$ ,  $N_2 =  etc. are monodentate ligands, they also act as bidentate ligands when they are attached to two separate metal atoms making a bridge between them. Such ligands are called bridging ligands and the complexes thus formed are called bridged or polynuclear complexes. A bridging ligand must have at least two lone pairs of electrons which the ligand uses to get coordinated to two or more metal atoms. The polynuclear complex formed can be dinuclear, trinuclear etc.

# 7.3.3.2 Chelation

When coordination of two or more donor atoms from a polydentate ligand to a single central atom/ion takes place forming a closed or cyclic ring structure, it is called chelation and the ligand a chelating ligand. The close ring compound thus formed is called chelate or metal chelate (Chelos, Greek word means 'crab').

# Some important characteristics of chelates:

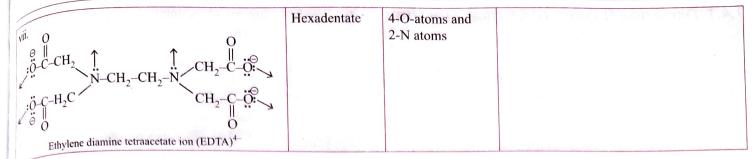
- a. Chelating effect: Chelating ligands form more stable complexes than the monodentate analogs. The complex ion/ compound having such ligands does not dissociate easily.
- b. Formation of rings: Generally the chelate complexes with 5- or 6-membered rings are more stable. Out of these, 5-membered rings are very stable when they involve saturated ligands, e.g., ethylenediamine which contains 5-membered stable ring structure. On the other hand 6-membered ring structures acquire maximum stability when they involve unsaturated ligands containing conjugate double bonds.
- c. Steric hindrance: Ligands with large groups form unstable rings than the ligands with smaller groups due to steric hindrance.

- d. Number of rings: The complex compound having maximum number of rings formed with the ligands is most maximum furfice of the stable and the former there are 3 rings while in the latter 5 rings.
- e. Entropy effect: The stability of the chelate complex is explained on the basis of entropy effect. To elaborate, let us take an example of ethylene diamine ligand (en). When one end of 'en' is coordinated, the probability of coordination of the other end is high because this end is bound to stay close to the central atom/ion. This shows that it is easier to form a chelate ring than forming coordinate bonds with two independent molecules. Thermodynamically, the increased stability due to chelation can be attributed to an increase in the degree of freedom of the system. Large changes in entropy but only small heat of reaction generally accompany the chelation process.

The number of donor atoms/ligating atoms present in the ligand molecule which are coordinating with the central atom/ion indicates the denticity of the ligand (Table 7.5).

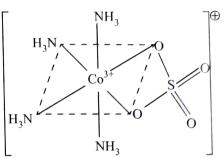
Table 7.5 Some examples of chelating ligands and number of donor atoms

Table 7.5 Some examples of chelating ligands a	Type of ligand	Donor atom	Examples
Ligand		2-O atoms	нн нн
i. $\begin{bmatrix} \vdots \ddot{O} \vdots & \ddot{O} \end{bmatrix}^{2-}$ ii. $\begin{bmatrix} O & \ddot{O} \\ \ddot{C} & \ddot{O} \vdots \\ \ddot{C} & \ddot{O} \end{bmatrix}^{2-}$ Carbonate ion  Oxalate ion or $[OX]^{2-}$	Bidentate or Didentate	2-O atoms	H <sub>2</sub> C N: N CH <sub>2</sub> H <sub>2</sub> C N: N CH <sub>2</sub> H <sub>2</sub> C N: N CH <sub>2</sub> H H H H  Bidentate chelation
iii. $H_2C$ — $NH_2$ iv. $H_2C$ — $NH_2$ iv. $H_2C$ — $NH_2$ $H_2C$ — $NH_2$ $H_2C$ — $H_2$	Bidentate or Didentate	2-N atoms	⊖:Cl. → Pt
v. $\ddot{N}H_2$ CH <sub>2</sub> CH <sub>2</sub> $\ddot{N}H$ CH <sub>2</sub> CH <sub>2</sub> $\ddot{N}H_2$ Diethylene triamine (dien)  or [N-(2-aminoethyl)-1, 2-ethane diamine)	Tridentate or Terdentate	3-N atoms	$H_2C$ $CH_2$ $H_2N: \longrightarrow H$ $CH_2$
vi. $\ddot{N}H_2(CH_2)_2\ddot{N}H$ ( $CH_2$ ) $_2\ddot{N}H$ (	Tetradentate	4-N atoms	$\begin{array}{c c} H_2C & CH_2 \\ \hline HN: & :NH & CH_2 \\ \hline H_2C & Pt & :NH_2 & CH_2 \\ \hline CH_2 & NH_2 & CH_2 \\ \hline [PtCl (trien)]^{2+} (Tetradentate chelation) \end{array}$



f. Flexidentate ligands: Certain ligands have more than one donor atoms like SO<sub>4</sub><sup>2-</sup>, CO<sub>3</sub><sup>2-</sup>, etc. which have more than one donor site/ligating atoms. Such ligands can behave as monodentate ligand in one complex and bidentate in another complex. Such ligands which show variable denticity in different complexes are known as flexidentate ligands. (It is not necessary for a polydentate ligand to use all its donor atoms for coordination.) For example:

 $[Co(NH_3)_5(SO_4)]^{\oplus}$  ion  $(SO_4^{2-}$  as monodentate ligand)



 $[Co(NH_3)_4(SO_4)]^{\oplus}$  ion  $(SO_4^{\ 2-}$  as bidentate ligand)

#### 7.4 COORDINATION NUMBER

The number of ligating atoms (of the ligands) that are directly bound to the central atom/ion is known as coordination number. It is equal to the number of sigma bonds formed between the ligands and central atom/ion.  $\pi$ -Bonds, if any, between the ligating atom and the central atom ion are not considered for the consideration of coordination number. Like CO, CN and N<sub>2</sub> may involve both  $\sigma$  and  $\pi$  bonding between the central atom/ion and the ligating atom, it is only number of  $\sigma$  bonds formed which are considered in determining the coordination number (Table 7.6).

### Tabe 7.6 Coordination number (CN) of some central metal atoms/ions (Note: CN = Denticity × no. of ligands)

#### A. Some examples of unidentate ligands

S.No.	Central metal atom/ions	CN	Complexes	Ligands
1.	Ag <sup>⊕</sup> , Cu <sup>⊕</sup> , Au <sup>⊕</sup>	2	$[Ag(NH_3)_2]^{\oplus}$	NH <sub>3</sub>
2.	Hg <sup>2+</sup>	3 and 4	$[\mathrm{HgI_3}]^{\ominus}$ , $[\mathrm{HgI_4}]^{2-}$	I <sup>©</sup>
3.	Cu <sup>2+</sup> , Pt <sup>2+</sup> , Ni <sup>2+</sup> , Mn <sup>2+</sup> , Pd <sup>2+</sup> , Zn <sup>2+</sup> , Ni <sup>0</sup>	4	[Cu(NH <sub>3</sub> ) <sub>4</sub> ] <sup>2+</sup> , [PtCl <sub>4</sub> ] <sup>2-</sup> , [Ni(CN) <sub>4</sub> ] <sup>2-</sup> , [MnBr <sub>4</sub> ] <sup>2-</sup> , [PdCl <sub>4</sub> ] <sup>2-</sup> , [ZnCl <sub>4</sub> ] <sup>2-</sup> , [Ni(CO) <sub>4</sub> ]	$NH_3$ , $Cl^{\Theta}$ , $CN^{\Theta}$ , $Br^{\Theta}$ , $Cl^{\Theta}$ $Cl^{\Theta}$ and $CO$ respectively
4.	Co <sup>2+</sup>	4 and 5	[Co(CN) <sub>5</sub> ] <sup>3-</sup> , [CoCl <sub>4</sub> ] <sup>2-</sup>	CN <sup>⊖</sup>
5.	Fe <sup>0</sup>	5	[Fe(CO) <sub>5</sub> ]	CO
6.	Fe <sup>2+</sup> , Fe <sup>3+</sup> , Co <sup>3+</sup> , Pt <sup>4+</sup> , Cr <sup>3+</sup> , Cr <sup>0</sup> , Ni <sup>2+</sup> , Ir <sup>3+</sup>	6	$\begin{aligned} & [\text{Fe}(\text{CN})_6]^4, [\text{Fe}(\text{CN})_6]^{3-}, [\text{Co}(\text{NH}_3)_6]^{3+}, \\ & [\text{PtCl}_6]^{2-}, [\text{Cr}(\text{H}_2\text{O})_6]^{3+}, [\text{Cr}(\text{CO})_6], \\ & [\text{NiF}_6]^{4-}, [\text{Ir}(\text{NH}_3)_6]^{3+} \end{aligned}$	$CN^{\ominus}$ , $CN^{\ominus}$ , $NH_3$ , $Cl^{\ominus}$ , $H_2O$ $CO$ , $F^{\ominus}$ and $NH_3$ respectively
7.	Mo <sup>4+</sup>	7	$[Mo(CN)_7]^{3-}$	CN <sup>⊖</sup>
8.	W <sup>4+</sup>	8	$[W(CN)_8]^4$	CN <sup>⊖</sup>

# B. Some examples of complexes with multidentate ligands.

- i.  $[Co(en)_3]^{3+}$ 
  - $CN = Didentate \times no. of ligands = 2 \times 3 = 6$
- **ii.**  $[Cr(dien)_2]^{3+}$

 $CN = Tridentate \times no. of ligands = 3 \times 2 = 6$ 

iii. [Mg(trien)Cl<sub>2</sub>]

 $CN = Tetradentate \times no. of ligands = 4 \times 1 + 2 = 6$ 

iv.  $[Mg(EDTA)]^{2-}$ 

 $CN = Hexadentate \times no. of ligands = 6 \times 1 = 6$ 

## 7.4.1 Oxidation Number of Central Atom/Ion

Oxidation number of the central atom in the coordination entity is defined as the charge it would bear if all the ligands were removed along with the electron pairs that were shared with the central atom. It is represented in numerals (Table 7.7).

**Table 7.7** Examples of important terms used in describing coordination compounds

Coordination compound	Central metal atom	Ligands	Oxida- tion no.	Geometrica shape	
Ni(CO) <sub>4</sub>	Ni	four CO	Zero	Tetrahedral	
$[Ni(Cl_4)]^{2-}$	Ni	four Cl <sup>⊖</sup>	II(2+)	Tetrahedral	
$[Ni(CN)_4]^{2-}$	Ni	four CN <sup>⊖</sup>	II (2+)	Tetrahedral	
$[Ni(H_2O)_6]^{2+}$	Ni	six H <sub>2</sub> O	II (+2)	Octahedral	
$[Co(NH_3)_6]^{3+}$	Со	six NH <sub>3</sub>	III (+3)	Octahedral	
[Co(CN) <sub>5</sub> F] <sup>3-</sup>	Co	five CN <sup>⊖</sup> one F <sup>⊖</sup>	III (+3)	Octahedral	
$\left[\mathrm{Ag(NH_3)_2}\right]^+$	Ag	two NH <sub>3</sub>	I (+1)	Linear	
[Cu(NH <sub>3</sub> ) <sub>4</sub> ] <sup>2+</sup>	Cu	four NH <sub>3</sub>	II (+2)	Square planar	

# 7.4.2 HOMOLEPTIC AND HETEROLEPTIC COMPLEXES

- a. Homoleptic complexes are those complexes in which central atom is coordinated with only one kind of ligand, e.g., [Fe(CN)<sub>6</sub>]<sup>3-</sup>.
- b. Heteroleptic complexes are those in which central atom is coordinated with more than one kind of ligands, e.g., [Fe(H<sub>2</sub>O)<sub>5</sub>NO]<sup>2+</sup>.

# 7.4.3 HOMONUCLEAR AND POLYNUCLEAR OR BRIDGED COMPLEXES

Complexes in which only one metal is present are known as homonuclear complexes, e.g.,  $\left[\text{Co(NH}_3)_6\right]^{3+}$  and  $\left[\text{Co(NH}_3)_4\text{Cl}_2\right]^{\oplus}$ .

Complexes in which more than one metal atom is present are known as polynuclear or bridged complexes. These complexes are formed by bridging ligands. These complexes formed can be dinuclear, trinuclear etc. For example,

$$\begin{bmatrix}
(H_2O)_4 & Fe & OH \\
OH & Fe & (H_2O)_4
\end{bmatrix}^{4+}$$

$$CO & CO & CO \\
OC & Mn & Mn & CO$$

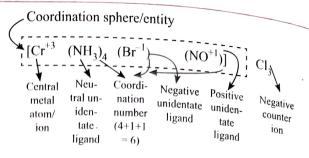
$$CO & CO & CO$$

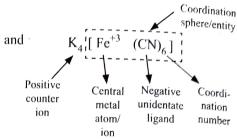
$$CO & CO & CO$$

$$Mn & CO$$

$$CO & CO$$

Various terms discussed above may be illustrated by taking some examples of coordination compounds, e.g.





#### ILLUSTRATION 7.1

Why  $\mathrm{NH_3}$  form coordinate complex, while the isoelectronic species  $\mathrm{CH_4}$  does not.

Sol. NH<sub>3</sub> has a lone pair of electron on N hence, it can act as a ligand and form coordinate complex whereas in CH<sub>4</sub>, C has no lone pair of electrons present on it, hence it cannot form complex.

#### ILLUSTRATION 7.2

Calculate the oxidation number of Ni ion [Ni(H<sub>2</sub>O)<sub>6</sub>]<sup>2+</sup>].

Sol. Oxidation number is calculated as follows:

Charge on complex ion = +2

Let charge on Ni = x

Charge on  $H_2O = O$ 

 $\Rightarrow x + 6 \times (0) = +2$ 

 $\Rightarrow x = 2+$ 

Hence oxidation number of Ni is II.

### ILLUSTRATION 7.3

Calculate the oxidation number of Ni in K<sub>2</sub>[Ni(CN)<sub>4</sub>].

15.

Sol. Let the charge on Ni be x

Charge on  $CN^{\ominus} = -1$ 

$$K_2[Ni(CN)_4] \rightarrow 2K^{\oplus} + [Ni(CN)_4]^{2-}$$

Charge on complex ion,  $[Ni(CN)_4]^{2-} = -2$ 

$$\Rightarrow$$
  $x + 4 \times (-1) = -2$ 

 $\Rightarrow$  x = +2

.. Oxidation number of Ni is II.

# ILLUSTRATION 7.4

What is the coordination number and oxidation state of Al in the complex  $[Al(H_2O)_4(OH)_2]^{\oplus}$ ?

**Sol.** Coordination number of Al in  $[Al(H_2O)_4(OH)_2]^{\oplus}$  is 6. To calculate oxidation state of Al in  $[Al(H_2O)_4(OH)_2]^{\oplus}$  Charge on  $H_2O$  is 0 (zero) and on OH is -1.

Let the charge on Al be x.

$$\int_{0}^{et} \frac{the \, charge}{x + 0 \times 4 + (-1) \times 2 = +1}$$

Oxidation state of Al in  $[Al(H_2O)_4(OH)_2]^{\oplus}$  is + 3.

# ILLUSTRATION 7.5

In the complex, [Fe(H<sub>2</sub>O)<sub>5</sub>Cl]Br, identify

Ligands and their charges.

Charge of the central ion in the complex.

What would happen if AgNO3 is added to the compound at

In complex [Fe(H<sub>2</sub>O)<sub>5</sub>Cl]Br, the complex ion is [Fe(H,O)5Cl]<sup>⊕</sup>

a. Ligands are  $5H_2O$  and  $Cl^{\odot}$ .

H,O is neutral ligand, whereas Cl<sup>⊕</sup> has one negative charge.

h. Let the charge on the central ion in the complex be x.

$$x + 0 \times 5 + (-1) = +1$$

$$x = +2$$

i.e. charge on Fe in [Fe(H<sub>2</sub>O)<sub>5</sub>Cl]<sup>\operatorname{O}</sup> is +2.

c.  $[Fe(H_2O)_5Cl]Br + AgNO_3 \rightarrow [Fe(H_2O)_5Cl]NO_3 + AgBr$ On addition of AgNO3 to the compound one mole of AgBr will be precipitated.

# 7.5 NOMENCLATURE OF COORDINATION COMPOUNDS

Coordination compounds are considered to be produced by addition reactions. They are therefore named on the basis of 'additive principle'. The name is built up around the central atom just as the coordination entity is built up around the central atom. For example, addition of ligands to a central atom:

 $(0^{3+} + 6NH_3 \longrightarrow [Co(NH_3)_6]^{2+},$  addition of ligands name to the central atom/ion is hexaamminecobalt(III).

### 7.5.1 Rules for Writing the Formulae for MONONUCLEAR COORDINATION COMPOUND

Sequence of symbols within the coordination formula is governed by the following rules:

- a. The central atom is listed first followed by the ligands.
- b. The ligands are listed in alphabetical order of the ligating atoms (charge of the ligand is not considered when deciding the order and the charge of the ligand is not written in the formula).
- c. The formula for the entire coordination entity is enclosed is square brackets.
- d. When the ligands are polyatomic (i.e. contain more than one atom) their formulae are enclosed in parentheses. Ligand abbreviations are also enclosed in parentheses.
- e. No space is kept between representations of ionic species within the formula.
- f. When the formula of a charged coordination entity is to be written without the counter ion, the charge of the

- coordination entity is written outside the square bracket as a right superscript. For example  $[Co(NH_2)_6]^{3+}$ ,  $[Co(CN)_6]^{3-}$
- g. Structural modifiers such as cis, trans etc. if present are given in lower case as an italicised prefix. It is connected to the formula by a hyphen.
- h. Finally a counter ion could be added to the coordination entity to form coordination compound. If counter ion is positively charged species, it is written in front of the formula of coordination entity, and if it is a negatively charged species, it is written after the formula of the coordination entity. No space is left between the counter ion and the coordination entity.

#### Note:

- A single letter symbol always precedes a two-letter symbol with the same initial letter, e.g. B before Be; O before OH, the group NH, is treated as a single symbol and so is listed after Na.
- Where the entities to be arranged in a formula are polyatomic:
  - a. The order of citation is decided by selecting the first symbol in the formula of a polyatomic group. For example, C5H5, SCN, NO2 and OH are ordered under C, S, N and O respectively.
  - b. If the first symbols are the same, the symbol with the lesser right index is cited first, e.g. NO2 precedes N2O2.
  - c. If this still does not discriminate, the subsequent symbols are used alphabetically and numerically to define the order, e.g. NH, precedes NO, which precedes NO,
  - d. To summarise and exemplify, the order of citation of some nitrogen-containing compounds is:  $N^{3-}$ ,  $NH_2^{\odot}$ ,  $NH_3^{\odot}$ ,  $NO_2^{\odot}$ ,  $NO_3^{\odot}$ ,  $N_2O_2^{2-}$ ,  $N_3^{\odot}$

For example,

 $\textbf{i.} \quad [\text{Al}(\text{OH})(\text{OH}_2)_5]^{2^+} \qquad \quad \textbf{ii.} \ [\text{PtCl}_2(\text{NH}_3)(\text{py})]$ 

iii.  $[Co(NH_3)_5(N_3)]^{2-}$ 

iv. [PtBrCl(NH<sub>3</sub>)(NO<sub>5</sub>)]<sup>©</sup>

v.  $[Co(en) F_2 (NH_3)_3]^{\oplus}$ , is written as  $[CoF_2(NH_2CH_2CH_2NH_2)(NH_3)_2]^{\oplus}$ 

i. Ionic charges and oxidation numbers: If the formula of a charged coordination entity is to be written without that of the counter ion, the charge is indicated outside the square bracket as a right superscript, with the number before the sign. The oxidation number of a central atom may be represented by a Roman numeral, which should be placed as a right superscript on the element symbol.

#### Examples:

i.  $[PtCl_6]^{2-}$  ii.  $[Cr^{lll} Cl_3(OH_2)_3]$  iii.  $[Cr(OH_2)_6]^{3+}$  iv.  $[Fe^{ll}(CO)_4]^{2-}$ 

v.  $[Cr^{III}(NCS)_4(NH_3)_5]^{\Theta}$ 

## 7.5.2 RULES FOR WRITING THE NAME OF MONONUCLEAR COORDINATION COMPOUND

The rules as recommended by IUPAC (International Union of Pure and Applied Chemistry), revised in 2005, being followed while naming a mononuclear coordination compound are as follows:

- i. If the coordination compound is molecular or non-ionic a single word name is given.
- ii. If the coordination compound is in the form of salt or ionic, name of the cation is given first, followed by the name of the anion in accordance with the usual nomenclature scheme. A space is left between the cationic and anionic part.
- iii. In the coordination entity, name of the ligand is written first followed by the name of central metal atom/ion.
- iv. Order of naming ions: The positive ion (cation) is named first followed by the negative ion (anion) irrespective of whether cation is complex or anion is complex. The complex part is written as one word e.g., [Co(NH3)6]Cl3, hexaamminecobalt(III) chloride.
- v. Naming of ligands: Different types of ligands are named differently (refer to Table 7.8).
  - a. Neutral ligands: These type of ligands have no special ending and are used as such except for NH3 (ammine), H,O (aqua), CO (carbonyl), CS (thiocarbonyl) and NO (nitrosyl).
  - b. Positive ligands: These type of ligands are used as such. These generally end in –ium, e.g.,  $H_2N - NH_3^{\oplus}$

- (hydrazinium), NO<sup>⊕</sup> (nitrosonium), NO<sub>2</sub><sup>⊕</sup> (nitronium)
- c. Negative ligands (organic or inorganic): These type of ligands end in '-O' e.g.,  $CN^{\ominus}$  (cyano),  $Cl^{\ominus}$  (chloro),  $NO_2^{\ominus}$  (nitro),  $O_2^{2-}$ (oxo)  $O_2^{2-}$ (peroxo),  $O_2^{\ominus}$ (superoxo). If the name of the anionic ligands ends in -ide, -ite or -ate, the last 'e' is replaced by 'O' giving -ido, -ito or ato e.g.  $SO_4^{2-}$  (sulphato),  $NH_2^{\Theta}$  (amido),  $ONO^{\Theta}$  (nitrito)
- d. Organic ligands: Organic free radicals are given their own names, e.g. CH<sub>3</sub> (methyl), (C<sub>2</sub>H<sub>5</sub>) (ethyl). For organic neutral molecules, their names are used. e.g.,  $P(C_6H_5)_3$ , triphenyl phosphine,  $C_6H_5N$  pyridine (py) etc. (refer Table 7.8).

Enclosing marks '()' are required for (a) neutral and Note: cationic ligand names (however, common ligands such as aqua, ammine, carbonyl, nitrosyl, methyl, ethyl, etc., do not require enclosing marks, unless there is ambiguity); (b) for inorganic anionic ligands containing numerical prefixes (such as triphosphato); (c) for any compositional name (such as carbon disulfide); (d) for any substituted organic ligand (even if there is no ambiguity in its use); (e) and wherever necessary to avoid ambiguity.

Table 7.8 List of neutral, positive and negative ligands

Denticity	neutral, positive and nega			Name of the ligand in the complex	Donor atom	
Neutral ligands	Water	H <sub>2</sub> O	0	Aqua/aquo	0	
	Ammonia	NH <sub>3</sub>	0	Ammine	N	
Strain, St.	Carbon monoxide	CO	0	Carbonyl	С	
	Nitrogen oxide	NO	0	Nitrosyl	N -	
0	Thiocarbonyl	CS	0	Thiocarbonyl	S	
	Thionitrosyl	NS	0	Thionitrosyl	N	
Monodentate	Pyridine (py)	C <sub>5</sub> H <sub>5</sub> N	0	Pyridine (py)	N	
	Methyl amine	CH <sub>3</sub> NH <sub>2</sub>	0	Methylamine	N	
	Dinitrogen	$N_2$	0	Dinitrogen	N	
	Dioxygen	$O_2$	0	Dioxygen	0	
	Phosphine	$PH_3$	0	Phosphine	P	
	Urea	$\begin{matrix} \mathrm{O} \\ \mathrm{H_2N-C-NH_2} \end{matrix}$	0	Urea	0	
	Thio-urea(tu)	$\begin{array}{c} \mathbf{S} \\ \mathbf{H}_2\mathbf{N} - \mathbf{C} - \mathbf{N}\mathbf{H}_2 \end{array}$	0	Thio-urea	S	
	Triphenylphosphine	Ph <sub>3</sub> P	0	Triphenylphosphine	P	
	Acetone	CH <sub>3</sub> COCH <sub>3</sub>	0	Acetone	O	
Bidentate	Ethylenediamine (en) (a bidentate ligand)	NH <sub>2</sub> (CH <sub>2</sub> ) <sub>2</sub> NH <sub>2</sub>	0	Ethylenediamine (en)	2 N-atoms	
Tridentate	Diethylene triamine (dien)	$\begin{array}{ccc} \mathbf{H_2C} & \ddot{\mathbf{N}} \mathbf{H} - \mathbf{CH_2} \\   & &   \\ \mathbf{H_2C} - \ddot{\mathbf{N}} & \ddot{\mathbf{N}} - \mathbf{CH_2} \\ \mathbf{H_2} & \mathbf{H_2} \end{array}$	0	Diethylene triamine (diene)	3 N-atoms	

Tetradentate	Triethylene tetramine (trien)	$ \begin{array}{c c} H_{2}C - \ddot{N}H(CH_{2})_{2}\ddot{N}H_{2} \\ H_{2}C - \ddot{N}H(CH_{2})_{2}\ddot{N}H_{2} \end{array} $	0	Triethylene tetramine (trien)	4N-atoms
		Positive ligands			
Monodentate	Nitrosonium ion	NO <sup>⊕</sup>	+1	Nitrosonium	N
Monodentare	Nitronium ion	NO₂ <sup>⊕</sup>	+1	Nitronium	N
	Hydrazinium ion	NH <sub>2</sub> NH <sub>3</sub> <sup>⊕</sup>	+1	Hydrazinium	N
		Negative ligands			
Monodentate	Hydride ion	$\mathrm{H}^{\odot}$	-1	Hydrido	Н
ile.	Oxide ion	$O^{2-}$	-2	Oxo	О
	Peroxide ion	$O_2^{2-}$	-2	Peroxo	0
	Perhydroxide ion	$O_2H^{\odot}$	-1	Perhydroxo	0
	Hydroxide ion	⊙ OH	-1	Hydroxo	О
	Fluoride ion	F <sup>⊙</sup>	-1	Fluoro (fluorido)	F
	Chloride ion	Cl <sup>⊖</sup>	-1	Chloro (chlorido)	Cl
	Bromide ion	Br <sup>©</sup>	-1	Bromo (bromido)	Br
	Iodide ion	I <sup>©</sup>	-1	Iodo (iodido)	1
	Acetate ion	CH <sub>3</sub> COO <sup>©</sup>	-1	Acetato (acetatido)	0
	Cyanide ion $\frac{\text{CH}_3\text{CO}}{\text{CN}^{\odot}}$		-1	Cyano (cyanido)	С
	Isocyanide ion	$N^{\oplus} \equiv C^{\ominus}$	-1	Isocyano	N
	Sulphite ion	SO <sub>3</sub> <sup>2-</sup>	-2	Sulphito	0
	Sulphide ion	S <sup>2-</sup>	-2	Sulphido or thio	S
	Hydrogensulphite ion	HSO₃ <sup>⊖</sup>	-1	Hydrogensulphito	O
	Amide ion	NH <sub>2</sub> <sup>©</sup>	-1	Amido	N
		NH <sup>2-</sup>	-2	Imido	N
	Imide ion	NO <sub>3</sub> <sup>©</sup>	-1	Nitrato	N
	Nitrate ion Nitro ion	$NO_2^{\ominus}(M \leftarrow N \downarrow 0)$	-1	Nitro (nitrito-N)	N
	Nitrito ion	$ONO^{\odot} (M \leftarrow O-N=O)$	-1	Nitrito (nitrito-O)	0
		N <sup>3-</sup>	-3	Nitrido	N
	Nitrido ion Azide ion	N <sub>3</sub> <sup>©</sup>	-1	Azido	N
		CNO <sup>©</sup>	<del>-</del> 1	Cyanato	0
	Cyanate ion	OCN <sup>©</sup>	-1	Isocyanato	N
	Isocyanate ion	SCN (M ← SCN)	-1	Thiocyanato	S
	Thiocyanate ion		-1	Isothyiocyanato	N
	Isothiocyanate ion	<sup>©</sup> NCS (M ← NCS)	-1	Hydrogencarbonato	0
Bidentate	Hydrogen carbonate ion  Acetyl acetonate ion			Acetylacetonato (Acac)	2 O-atom
	Glycinate ion	NH <sub>2</sub> -CH <sub>2</sub> -COO <sup>⊙</sup>	-1	Glycinato(gly)	1 N-atom and 1 O-atom
	Sulphate ion	SO <sub>4</sub> <sup>2-</sup>	-2	Sulphato	2 O-atom
	Thiosulphate ion	S <sub>2</sub> O <sub>3</sub> <sup>2-</sup>		Thiosulphato	2 O-atom

	Dimethylglyoxime	O <sup>©</sup> CH <sub>3</sub> C=N: CH <sub>3</sub> C=N: OH	-1	Dimethylglyoxiomato	2 N-atom
	Oxalate ion	$C_2O_4^{2-}$	-2	Oxalato	2 O-atom
	Carbonate ion	CO <sub>3</sub> <sup>2</sup>	-2	Carbonato	2 O-atom
Pentadentate	Ethylenediamine triacetate ion	CH <sub>2</sub> −Ñ(CH <sub>2</sub> COO <sup>©</sup> ) <sub>2</sub>     CH <sub>2</sub> −ÑHCH <sub>2</sub> COO <sup>©</sup>	-3	(EDTA <sup>3-</sup> )	2 N-atoms and 3 atoms
Hexadentate	Ethylenediamine tetraacetate ion	$\begin{array}{c} \operatorname{CH_2\overset{\bullet}{N}(CH_2CO_2^{\odot})_2} \\ \operatorname{CH_2\overset{\bullet}{N}(CH_2CO_2^{\odot})_2} \end{array}$	-4	(EDTA <sup>4</sup> )	2 N-atoms and 4 O-atoms

vi. Within the coordination sphere, if more than one kind of ligands are present, they are listed in alphabetical order (irrespective of their charge) before the name of the central atom. Numerical prefixes which indicate the number of ligands are not considered in determining that order.

For example,

 $[PtClBr(NO_2)(NH_3)]^{\odot}$ 

Amminebromidochloridonitroplatinate (II)

[CoCl(NH<sub>2</sub>)<sub>5</sub>]<sup>2-</sup>

Pentaamminechloridocobaltate (III)

- vii. Prefixes: Number of ligands in the coordination entity is indicated as numerical prefix. Two types of numerical prefixes are used.
  - di, tri, tetra, penta etc. (mono is generally omitted). Multiplicand is not enclosed in parentheses. This is used for simple ligands.

For example,  $2 \text{ Cl}^{\odot} \longrightarrow \text{dichlorido}$   $3 \text{ NH}_3 \longrightarrow \text{triammine}$ 

b. bis, tris, tetrakis, pentakis etc. Multiplicand is enclosed in parenthesis. This is used for complex ligands, i.e., when the name of the ligand is lengthy or complicated (polysyllabic or multiplicative prefixes are already present in the ligand)

Bis(methylamine)

$$\begin{pmatrix} CH_2 - NH_2 \\ CH_2 - NH_2 \end{pmatrix}_3$$
 Tris (1, 2-ethanediamine)
$$\begin{pmatrix} H_3C - C - C - CH_3 \\ \parallel & \parallel \\ N & N \\ HO & O \end{pmatrix}_2$$

Bis(dimethylglyoximato)

viii. The final vowel of the numerical prefix is not omitted. (mono is an exception)

 $mono + oxide \longrightarrow (monoxide)$ 

Example:

 $(NH_3)_4$  Tetraammine  $(O^{2-})_4$  Tetraoxide

The complex  $[CoCl_2(NH_3)_4]^{\oplus}$  is Tetraamminedichloridocobalt (III)

ix. The oxidation state of the central metal atom/ion is expressed in roman numerals, which is added at the end of the name of metal atom/ion and enclosed in bracket. No positive sign is used. For example,

[Co(NH<sub>3</sub>)<sub>6</sub>]<sup>2+</sup> Hexaamminecobalt (III) ion

x. When the coordination entity is anionic or negatively charged the name of the central metal atom/ion ends with suffix 'ate', i.e., the name of coordination entity ends in 'ate'.

For certain elements their latin name is used, e.g.,

Example	Name in positive/ neutral complex	Name in anionic or negative complex
Ag	Silver	Argentate
Pb	Lead	Plumbate
Au	Gold	Aurate
Hg	Mercury	Mercurate or hydra- zinate
Ni	Nickel	Nickelate
Fe	Iron	Ferrate

xi. If the coordination entity is positively charged or neutral, it has no special ending. For example,

 $[Co(CN)_6]^{3-}$  Hexacyanocobaltate (III) ion.

xii. Stereochemical descriptors: For coordination number greater than one, different geometrical arrangements of the atoms attached to the central metal ion are possible. A descriptor is used to differentiate between isomers. The descriptor is indicated as an italicized prefix, in lower case. It is connected to the name by a hyphen.

For example, 
$$\begin{bmatrix} H_3N \\ H_3N \end{bmatrix} Pt \begin{bmatrix} Cl \\ Cl \end{bmatrix}$$

is named as cis-diaminedichloridoplatinum (II)

xiii. Naming of the optical isomers: Dextro and Levorotatory optically active compounds are respectively designated either by (+) and (-) or by d- and l; e.g., dextrorotating

 $K_3[Cr(OX)_3]$  is named as potassium (+) trioxalatochromate (III) or potassium d-trioxalatochromate (III).

Naming of the linkage isomers: If necessary, the point of attachment of the ligand to the central metal is expressed by the symbol of element attached in italics after the name of the ligand and separated by a hyphen.

Ligand	Donor atom	Name of the ligand
←:SCN <sup>©</sup>	S	Thiocyanato-S
·NCS	N	Thiocyanato-N
←:CN <sup>©</sup>	С	Cyano-C
←:NC <sup>⊖</sup>	N	Cyano-N
$\begin{bmatrix} S & C - C & S \\ O & C \end{bmatrix}^{2-}$ $\downarrow$	0,0	Dithioxalato- O-O'
$\begin{bmatrix} S & \\ O & C & \\ C & $	O, S	Dithioxalato- O-S
$\begin{bmatrix} \uparrow & \uparrow \\ \ddot{S} & C - C & \ddot{S} \\ 0 & C - C & O \end{bmatrix}^{2-}$	S, S	Dithioxalato- S-S'

For example:  $[Co(NH_3)_5 (NO_2)]^{2+}$  has two isometric forms having red and yellow colours.

- 1. The red colour isomer  $[Co(NH_3)_5 (ONO_2)]^{2+}$  is named as pentaamminenitrito-O-cobalt (III).
- 2. The yellow isomer  $[Co(NH_3)_5 (NO_2)]^{2^+}$  is named as pentaamminenitrito-N-cobalt (III)

#### 7.5.3 BRIDGING LIGAND

Lis defined as the ligand which bounds to two or more central arms simultaneously giving a polynuclear complex, e.g.

 $[NH_3)_5$  Co-OH-Co(NH<sub>3</sub>)<sub>5</sub>]Cl<sub>5</sub> (- OH<sup> $\odot$ </sup> acts as bridging ligand)

When bridging ligand is present within the complex, following points are noted for the nomenclature of these complexes:

- i. Bridging ligand is expressed by greek letter '\mu' which is added immediately before the name of the ligand and separated by a hyphen.
- ii. The number of bridging ligands are expressed as:

di-μ (Two bridging ligands)

Tri-μ (Three bridging ligands)

bis- $\mu$  (Two polysyllabic bridging ligands)

- ili. The bridging ligands along with non-bridging ligands are generally written in alphabetical order unless the symmetry of the complex permits the simpler name by the use of multiplicative prefixes.
- iv. If the same type of ligand is acting as bridging as well as non-bridging ligand, the bridging ligand is expressed first. Following examples illustrate the above points:

$$\mathbf{a.} \quad [(\mathring{N}H_3)_5 \text{Co}^{+3} - \bar{O}^{1}H - \mathring{Co}(\mathring{N}H_3)_5]^{+5} \text{Cl}_5^{-1 \times 5}$$

is given the name as

 $\mu$ -hydroxo-bis (pentaamminecobalt (III)) chloride

**b.** 
$$\frac{\bar{c}_{1}^{1}}{Et_{3}\hat{p}} > Pt^{+2} < \frac{\bar{c}_{1}^{1}}{\bar{c}_{1}^{1}} > Pt^{+2} < \frac{\bar{c}_{1}^{1}}{\hat{p}_{Et_{3}}}$$

(cis-di-μ-chloridobis(chlorotriethylphosphineplatin um (II))

Tri- $\mu$ -carbonyl bis(tricarbonyliron(0))

#### 7.5.4 POLYNUCLEAR COMPLEXES

Polynuclear complexes having M–M bond can be symmetrical or unsymmetrical. In such complexes the rules followed to write the name of the complex are as follows:

i. In case of symmetrical complex, the names are generally given with the use of multiplicative prefixes like di-, tri-, tetra-, etc.

For example,  $[(\mathring{CO})_5 \mathring{Mn} - \mathring{Mn}(\mathring{CO})_5]$ Bis (pentacarbonylmanganese(0))

ii. In case of unsymmetrical complex, one of the central atom and ligands bonded to it are considered as the ligand to the other central atom.

For example,  $[(C\mathring{O})_4\mathring{C}O - \mathring{R}e(\mathring{C}O)_5]$ 

Pentacarbonyl (tetracarbonylcobalt(O))ruthenium (0)

# 7.5.5 STABLE OXIDATION STATE (OS): SOME OF THE TRANSITION METALS OF THE THREE SERIES

These stable OS would be helpful to find the oxidation states of the metal ions while naming complexes having cation and anion both as complexes.

#### i. First transition series:

Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
+3	+2,	+2,	+2,	+2,	+2,	+2,	+2,	+1,	+2
	+3	+3	+3	+3	+3	+3	+3	+2	
	+4	+4,	+6	+4,					
		+5		+7					

#### ii. Second transition series:

1	Y	Zr	Nb	Mo	Te	Ru	Rh	Pd	Ag	Cd
	+3	+4	+3,	+6	+4,	+3	+3	+2,	+1	+2
			+5		+6			+4		
					+7				w chi	

#### iii. Third transition series:

La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg
+3	+4	+5	+6		+3, +4				
4-1.				+6	+4	+3	+4	+3	+2
			4 ·	+7	+6	+4			

Table 7.9 IUPAC name of some complexes

a.	Complex cation	IUPAC name
1.	[Co(NH <sub>3</sub> ) <sub>6</sub> ]Cl <sub>3</sub>	Hexaamminecobalt(III) chloride
2.	[Cr Cl <sub>2</sub> (H <sub>2</sub> O) <sub>4</sub> ] NO <sub>3</sub>	Tetraaquadichloridochromium (III) nitrate
3.	[CoCl(NO <sub>2</sub> )(NH <sub>3</sub> ) <sub>4</sub> ]NO <sub>3</sub>	Tetraamminechloridonitrito-N-cobalt(III) nitrate
4.	[Cr(en) <sub>3</sub> ]Cl <sub>3</sub>	Tris(1,2-ethanediamine)chronium(III)chloride
5.	[CoCl <sub>2</sub> (en) <sub>2</sub> ] (SO <sub>4</sub> ) <sub>2</sub>	Dichlorido(1,2-ethanediamine)cobalt(II) sulphate
6.	$Na_3[Fe(C_2O_4)_3]$	Sodium trioxalatoferrate(III)
7.	[CoBr(NH <sub>3</sub> ) <sub>4</sub> (H <sub>2</sub> O)](NO <sub>3</sub> ) <sub>2</sub>	Tetraammineaquabromidoocobalt(III) nitrate
8.	[Cr(H <sub>2</sub> O) <sub>6</sub> ]Cl <sub>3</sub>	Hexaaquachromium(III) chloride
9.	[CoCl(ONO)(en) <sub>2</sub> ] <sup>⊕</sup>	Chloridobis(1,2-ethanediamine)nitrito-O-cobalt(III) ion
10.	[CrCl <sub>2</sub> (H <sub>2</sub> O) <sub>4</sub> ]Cl	Tetraaquadichloridochromium(III) chloride
11.	[Co(CO <sub>3</sub> )(NH <sub>3</sub> ) <sub>5</sub> ]Cl	Pentaamminecarbonatocobalt(III) chloride
12.	[Ir(en) <sub>2</sub> (NH <sub>3</sub> ) <sub>2</sub> ]Cl <sub>3</sub>	Diammine bis(1,2-ethanediamine)iriduim(III) chloride
13.	[CoCl(NH <sub>3</sub> ) <sub>4</sub> NO <sub>2</sub> ]ClO <sub>4</sub>	Tetraamminechloridonitritocobalt(III) perchlorate
14.	[Ag(NH <sub>3</sub> ) <sub>2</sub> ]Cl	Diamminesilver(I) chloride
15.	$[CoBrCl(en) (ONO)_2]^{\oplus}$	Bromidochlorido(1,2-ethanediamine)dinitrito-O-cobalt (III) ion
16.	[Co(en) (NH <sub>3</sub> ) <sub>2</sub> BrCl] NO <sub>3</sub>	Diaminebromidochlorido(ethylenediamine)cobalt(III)nitrate
17.	[CoCl(en)₂ONO] <sup>⊕</sup>	Chloridobis(ethylenediamine) nitrito-O-cobalt(III) ion.
18.	$[Co(NH_2)_2(NH_3)_4]OC_2H_5$	Diamidotetraamminecobalt(III) ethoxide
19.	[CoN <sub>3</sub> (NH <sub>3</sub> ) <sub>5</sub> ]SO <sub>4</sub>	Pentaammineazidocobalt(III) sulphate
20.	$[Co(en)_3]_2 (SO_4)_3$	Tris(1,2-ethanediamine)cobalt(III) sulphate
21.	[Cr(H2O)6]Cl3	Hexaaquachromium(III) chloride
22.	[Ru(NH <sub>3</sub> ) <sub>5</sub> N <sub>2</sub> ]Cl <sub>2</sub>	Pentaamminedinitrogenruthenium(II) chloride
23.	[Co(NCS)(NH <sub>3</sub> ) <sub>5</sub> ]Cl <sub>2</sub>	Pentaammine-thiocyanato-N-cobalt(III) chloride
24.	[Co(ONO)(NH <sub>3</sub> ) <sub>5</sub> )]SO <sub>4</sub>	Pentaamminenitrito-O-cobalt(III) sulphate
b.	Complex anions	IUPAC name
25.	$K_3[Fe(C_2O_4)_3]$	Potassium trioxalatoferrate(III)
26.	K <sub>2</sub> [CO(CN) <sub>5</sub> (NO)]	
27.	K[PtCl <sub>3</sub> (NH <sub>3</sub> )]	Potassium pentacyanidonitrosylcobaltate(III)  Potassium amminetrichloridoplatinate(II)
28.	Na <sub>2</sub> [CrOF <sub>4</sub> ]	
29.	Na <sub>2</sub> [SiF <sub>6</sub> ]	Sodium tetrafluoridooxochromate (IV)
30.	[Hg[Co(SCN) <sub>4</sub> ]	Sodium hexafluoridosilicate(IV)
31.	K <sub>4</sub> [NiCN) <sub>4</sub> ]	Mercuric tetrathiocyanatocobaltate(II)
32.	Dextro $K_3[Ir(C_2O_4)_3]$	Potassium tetracyanonickelate(0)
33.	Li[AlH <sub>4</sub> ]	Potassium d-trioxalatoiridate(III)
34.	$(NH_4)_2[Pt(SCN)_6]$	Lithium tetrahydridoaluminate(III)
35.	$K_3[Co(NO_2)_6]$	Ammonium hexathiocyanatoplatinate (IV)
		Potassium hexanitritocobaltate(III)
36.	$K_3[Co(NO_2)_c]$	
	$K_3[Co(NO_2)_6]$ (NH <sub>4</sub> ) [Cr(NH <sub>2</sub> ) <sub>3</sub> (NCS) <sub>4</sub> ]	Potassium hexanitritocobaltate(III)
37.	$(NH_4)$ [Cr $(NH_3)_2(NCS)_4$ ]	Ammonium diamminetetrathiocyanato-N-chromate(III)
37. 38.	$(NH_4) [Cr(NH_3)_2(NCS)_4]$ $[Co(H_2O)_3Cl_2(CO_3)]^{\Theta}$	Ammonium diamminetetrathiocyanato-N-chromate(III)  Triaquacarbonatodichloridocobaltate(III) ion
37. 38. 39.	$(NH_4) [Cr(NH_3)_2(NCS)_4]$ $[Co(H_2O)_3Cl_2(CO_3)]^{\ominus}$ $[Cr(NEt_2)_4]^{\ominus}$	Ammonium diamminetetrathiocyanato-N-chromate(III) Triaquacarbonatodichloridocobaltate(III) ion Tetrakisdiethylamidochromate(III) ion
36. 37. 38. 39. 40.	$(NH_4) [Cr(NH_3)_2(NCS)_4]$ $[Co(H_2O)_3Cl_2(CO_3)]^{\Theta}$ $[Cr(NEt_2)_4]^{\Theta}$ $K_2[OsCl_5N]$	Ammonium diamminetetrathiocyanato-N-chromate(III)  Triaquacarbonatodichloridocobaltate(III) ion  Tetrakisdiethylamidochromate(III) ion  Potassium pentachloridonitridoosmiate(VI)
37. 38. 39. 40.	$(NH_4) [Cr(NH_3)_2(NCS)_4]$ $[Co(H_2O)_3Cl_2(CO_3)]^{\ominus}$ $[Cr(NEt_2)_4]^{\ominus}$ $K_2[OsCl_5N]$ $K_3[Fe(CN)_6]$	Ammonium diamminetetrathiocyanato-N-chromate(III) Triaquacarbonatodichloridocobaltate(III) ion Tetrakisdiethylamidochromate(III) ion Potassium pentachloridonitridoosmiate(VI) Potassium hexacyanoferrate(III)
37. 38. 39.	$(NH_4) [Cr(NH_3)_2(NCS)_4]$ $[Co(H_2O)_3Cl_2(CO_3)]^{\Theta}$ $[Cr(NEt_2)_4]^{\Theta}$ $K_2[OsCl_5N]$	Ammonium diamminetetrathiocyanato-N-chromate(III) Triaquacarbonatodichloridocobaltate(III) ion Tetrakisdiethylamidochromate(III) ion

$Na_3[Ag(S_2O_3)_2]$	Sodium bis(thiosulphato)argentate(I)
$K[B(C_6H_5)_4]$	Potassium tetra(phenyl)borate(III)
K[SbCl <sub>5</sub> C <sub>0</sub> H <sub>5</sub> ]	Potassium pentachlorido(phenyl)antimonate(V)
$K[PtCl_3(C_2H_4)]$	Potassium trichlorido(ethylene) platinate(II)
$Na_2[Fe(CN)_5NO]$	Sodium pentacyanonitrosylferrate(II)
K <sub>3</sub> [Fe(CN) <sub>5</sub> CO]	Potassium carbonylpentacyanoferrate(II)
$Na_3[Co(NO_2)_6]$	Sodium hexanitrito-N-cobaltate(III)
$K_3[Al(C_2O_4)_3]$	Potassium trioxalatoaluminate(III)
$Ca_2[Fe(CN)_6]$	Calcium hexacyanoferrate(II)
Na[Co(CO) <sub>4</sub> ]	Sodium tetracarbonylcobaltate(-1)
$(NH_4)_3[Cr(NCS)_6]$	Ammonium hexathiocyanato-N-chromate(III)
$K_3[Cr(CN)_6]$	Potassium hexacyanochromate(III)

 $_{\text{Note:}}$  For  $CN^{\odot}$  either cyano or cyanido may be written.

Neutral complexes	IUPAC name
[Ni(CO <sub>4</sub> ]	Tetracarbonylnickel(O)
$[Co(NO_2)_3(NH_3)_3]$	Triamminetrinitrito-N-cobalt(III)
[PtCl2(NH3)2]	Diamminedichloridoplatinum(II)
[Cr(PPh <sub>3</sub> ) (CO) <sub>5</sub> ]	Pentacarbonyltriphenylphosphinechromium(O)
[Ni(dmg) <sub>2</sub> ]	Bis(dimethylglyoximato)nickel(II)
[Mn3(CO)2]	Dodecacarbonyltrimanganase(O)
[Cr(NH <sub>3</sub> )(NO <sub>2</sub> ) <sub>3</sub> ]	Triamminetrinitritochromium(III)
[CuCl <sub>2</sub> (CH <sub>3</sub> CH <sub>2</sub> ) <sub>2</sub> ]	Dichloridobis(methylamine)copper(II)
cis-[PtCl <sub>2</sub> (PEt <sub>3</sub> ) <sub>2</sub> ]	cis-dichloridobis(triethylphosphine)platinum(II)
No. of the last of	Diglycinatocopper(II)
$[Cu(gly)_2]$ $[CuCl_2(O=C(NH_2))_2]Cl_2$	Dichloridobis(urea)copper(II)

Complexes containing cationic and anionic ions	IUPAC name
The state of the s	Tetraamminedichloridoplatinum(IV) tetrachloridoplatinate(II)
[PtCl <sub>2</sub> (NH <sub>3</sub> ) <sub>4</sub> ] [PtCl <sub>4</sub> ]	Tetraamminedichloridocobalt(III) hexacyanidochromate(III)
$[\operatorname{CoCl}_{2}(\operatorname{NH}_{3})_{4}]_{3} [\operatorname{Cr}(\operatorname{CN})_{6}]$	Tetraammineplatinum(II) tetrachloridoplatinate(II)
[Pt(NH <sub>3</sub> ) <sub>4</sub> ] [PtCl <sub>4</sub> ]	Tris(1,2-ethanediamine) chromium(III) tetra-chloridoferrate(III)
$[Cr(en)_3]$ $[FeCl_4]_3$	Tetrakis(pyridine)platinum(II) tetrachloridoplatinate(II)
$[Pt(pv)_{a}][PtCl_{a}]$	Tetrakis(pyridine)piddinam(12) tetrakis(pyridine)piddinam(12)

	(4)/21 (4 - 4)	
е.	Bridge complexes	IUPAC name
72.	[(NH <sub>3</sub> ) <sub>5</sub> Cr–OH–Cr(NH <sub>3</sub> ) <sub>5</sub> ]Cl <sub>5</sub>	μ-Hydroxobis(pentaamminechromium(III) chloride
73.	$(H_2O)_4 \text{ Fe} OH Fe(H_2O)_4 (SO_4)_2$	Di-μ-hydroxobis(tetraaquairon(III) sulphate
74.	$ \begin{array}{c c} \hline (NH_3)_4CO & NH_2 \\ NO_2 & Co(NH_3)_4 \\ \hline (NO_3)_4 & OOOOOOOOOOOOOOOOOOOOOOOOOOOOOOOOOOO$	μ-Amido-μ-nitritobis(tetraamminecobalt(III)) nitrate
75.	$K_2 Ni $ $O=C-S$ $O=C-S/2$	Potassium bis(thiooxalato-O-O')nickelate(II)
76.	$\begin{bmatrix} S & O & Pt \\ O & S & O \end{bmatrix}^{2-}$	Thiosulphato-O-O'-thiosulphato-O-S-platinate(II) ion

77. $OC \longrightarrow Fe \longrightarrow CO \longrightarrow Fe$	CO CO CO Tris-μ-carbonylbis(tricarbonyliron(0))
78. $(C_6H_5)_3P$ $Pt$ $Cl$	$Pt = C1 \\ P(C_6H_5)_3 $ trans-Di- $\mu$ -chloridobis(chloridotriphenylphosphineplatinum(II)
79. [(CO) <sub>5</sub> Mn—Mn(CO)	Bis(pentacarbonylmanganese(0))
80. $ (H_3^{\circ}N)_4Cr^{+3} \underbrace{O_2^{-1}}_{O_2^{-2}} $	$\left(\operatorname{Cr}^{+3}(\operatorname{NH}_{3}^{o})_{4}\right)^{+3}$ Br <sub>3</sub> <sup>-3</sup> $\operatorname{Br}_{3}^{-3}$ $\operatorname{\mu-Peroxo-\mu-superoxobis(tetraamminechromium(III) bromide}$
81. $\left[ (NH_3)_4 Cr \underbrace{O_2}_{O_2} Cr (NH_3)_4 Cr \underbrace{O_3}_{O_3} Cr (NH_3)_4 Cr \underbrace{O_3}_{O$	NH <sub>3</sub> ) <sub>4</sub> (ClO <sub>4</sub> ) <sub>2</sub> Di-μ-peroxobis(tetraamminechromium(III)) perchlorate
82. $\left[ (\mathrm{H_2O})_4 \mathrm{Co} \overset{\mathrm{O_2}}{\mathrm{O_2}} \mathrm{Co} (\mathrm{O_2}) \right]$	H <sub>2</sub> O) <sub>4</sub> (BrO <sub>4</sub> ) <sub>4</sub> Di-μ-superoxobis(tetraaquacobalt(III)) perbromate

Table 7.10 Names and structures of some abbreviations used in complexes

S.No.	Abbreviations	Name and structure
1. •	acac <sup>⊜</sup>	O $O$ $O$ $O$ $O$ $O$ $O$ $O$ $O$ $O$
2.	acacH	OH O Acetylacetone [CH <sub>3</sub> -C=CH-C-CH <sub>3</sub> ]
3.	am	Ammonia (NH <sub>2</sub> )
4.	aq	Aqua (H <sub>2</sub> O)
5.	big	$\begin{array}{c c} \text{NH} & \text{N}^{\Theta} \\ \text{Biguanido ion } [\text{H}_2\text{N-C-NH-C-NH}_2] \end{array}$
6.	big H	NH NH  Biguanide [H <sub>2</sub> N-C=NH-C-NH <sub>2</sub> ]  Biguanide [H <sub>2</sub> N-C=NH-C-NH <sub>2</sub> ]
7.	dien	Diethylentries out
8.	DMG <sup>⊕</sup>	Diethylentriamine $(NH_2-(CH_2)_2-NH-(CH_2)_2-NH_2$ Dimethylglyoximatio ion $H_3C-C=N$ OH $H_3C-C=N$ O $\ominus$
9.	DMGH	Dimethylglyoxime H <sub>3</sub> C-C=N OH
10.	EDTA <sup>4-</sup>	$\begin{array}{c} H_{3}C-C=N \searrow OH \\ \\ Ethylenediaminetetraacetatoion \\ {}^{\Theta}OOC-H_{2}C \searrow N-(CH_{2})_{2}-N \swarrow \begin{array}{c} CH_{2}-COO^{\Theta} \\ \\ CH_{2}-COO^{\Theta} \end{array}$
11.	$EDTAH_4$	CH <sub>2</sub> -COO <sup>©</sup>
12.	en	Eurylenediaminetetraaceticacid
13.	eten	Ethylenediamine $ \text{N-ethylethylenediamine } [\text{H}_2\text{N-}(\text{CH}_2)_2\text{-NH-}\text{C}_2\text{H}_5] $
14.	gly <sup>©</sup>	
15.	glyH	Glycinato ion (NH <sub>2</sub> −CH <sub>2</sub> −COO <sup>©</sup> )
16.	IDA <sup>2-</sup>	Glycine
17.	IDA H <sub>2</sub>	<sup>©</sup> OOC-CH <sub>2</sub> -NH-CH <sub>2</sub> -COO <sup>©</sup> (Imidodiacetato ion)
18.	$OX^{2-}$	Imidodiacetic acid  Oxalato ion [ $^{\Theta}$ OOC-COO $^{\Theta}$ ]

	OMA		Coordination Compounds	7
19.	OXH <sub>2</sub>	Oxalic acid		
20.	tetraen	Tetraethylenepentamine		-
21.	trien	Triethylenetetramine		
22.	ph	Ortho-phenthroline		-
23.	pn	1, 2-Diaminepropane		-
24.	tn	1, 3-Diaminepropane		
_				1

7.11 Formulae of the coordination compounds

10.	Name	Formula 1
	Sodium pentacyanonitrosylferrate(III)	Formula No. III. +3 consts and 0r 2
 !.	Hexakis(ethanenitrile)iron(II) chloride	$Na_{2}[Fe^{+3}(CN^{-5})_{5}NO^{0}]^{-2}$
		[Fe(CH <sub>3</sub> CN) <sub>6</sub> ]Cl <sub>2</sub>
3.	Pentaamminedinitrogenruthenium(II) chloride	[Ru(NH3)5(N2)]Cl2
4.	Tetraethylammonium diamminetetrathiocyana- to-N-chromate(III)	(NEt) <sub>4</sub> [Cr(NH <sub>3</sub> ) <sub>2</sub> (NCS) <sub>4</sub> ]
5.	Triamminecarbonatodichlorido cobaltate(III) ion	$[\text{CoCl}_2(\text{CO}_3)(\text{NH}_3)_3]^{\Theta}$
6.	Ammonium hexathiocyanato-S-platinate(IV)	$\frac{(NH_4)_2[Pt(SCN)_6]}{(NH_4)_2[Pt(SCN)_6]}$
7.	trans-diamminedichloridoplatinum(II)	
	1	$\frac{H_3N}{Cl}$ $Pt$ $\frac{Cl}{NH_3}$
8.	Ammonium total	그는 그리고 그리는 이 이 이 이 아이를 가장하는 것이 되는 것이 없는데 그리는데 그리는데 그리는데 그리는데 그리는데 그리는데 그리는데 그리
0.	Ammonium tetraamminediisothiocyanato chromate(III)	$(NH_4) [Cr(NH_3)_4(NCS)_2]$
9.	Tetraamminechloridothiocyanato-N-cobalt(III)	
10.		[CoCl(NH <sub>3</sub> ) <sub>4</sub> (NCS)]NO <sub>3</sub>
11.	Tetrachlorido(1, 2-ethanediamine) platinum(IV)	$[PtCl_4(en)]$
12.	Sodium diamminetetracyanochromate(III)	$Na[(Cr(NH_3)_2(CN)_4]$
	Sodium ethylenediaminetetraacetato nickelate(II)	Na <sub>2</sub> [Ni(edta)]
13.	Potassium tetracyanonickelate(0)	$K_4[Ni(CN)_4]$
14.	Amminebromidochloridomethylamine platinum(II)	[PtBrCl(NH <sub>3</sub> )(CH <sub>3</sub> NH <sub>2</sub> )]
15.	cis-tetraamminedichloridocobalt(III) chloride	$\begin{bmatrix} CI & CI \\ CI & NH_3 \\ NH_3 \end{bmatrix} CI$ $\begin{bmatrix} NH_3 & NH_3 \\ NH_3 \end{bmatrix} CI$
16.	Tetraaquadichloridochromium(III) nitrate	[CrCl <sub>2</sub> (OH <sub>2</sub> ) <sub>4</sub> ]NO <sub>3</sub>
17.	Ammonium aquapentafluoridonickelate(IV)	(NH <sub>4</sub> ) [NiF <sub>5</sub> (H <sub>2</sub> O)]
18.	Bromidodichloridoididoplatinate(IV)	[PtBrCl <sub>2</sub> I]
19.	Magnesium hexacyanoferrate(II)	$Mg_2[Fe(CN)_6]$
20.	Potassium tetraoxoferrate (IV)	$K_4[Fe(O)_4]$
21.	Potassium tetrazidocobaltate(II)	$\frac{K_4[\Gamma c(O)_4]}{K_2[Co(N_3)_4]}$
22.	Dichloridobis (triphenylphosphine) nickel(II)	$\frac{R_2[Co(N_3)_4]}{[NiCl_2(PPh_3)_2]}$
23.	Chloridocarbonylbis(triphenylphosphine)	[IrClCO(PPh <sub>3</sub> ) <sub>2</sub> ]
24.	iridium(1)	[110100(17113)2]
~7.	Hexaamminecobalt(III) diamminetetrachlorido	$[\operatorname{Co(NH}_3)_6][\operatorname{CrCl}_4(\operatorname{NH}_3)_2]$
25.	chromate (III)	2 3/61 [O: O:4(14113/2]
26.	Hexaamminenickel(II) hexanitritocobaltate(III)	$[Ni(NH_3)_6 [Co(NO_2)_6]$
	Tetraamminedibromidocobalt(II) tetrachlororidozincate(II)	$[\operatorname{CoBr}_2(\operatorname{NH}_3)_4][\operatorname{ZnCl}_4]$
27.	Tetramminesulpheter 1 1 2000	2 3:42 43
	Tetramminesulphatocobalt(III) nitrate	$[\text{Co(NH}_3)_4(\text{SO}_4)]\text{NO}_3$

#### 7.22 Inorganic Chemistry

Triamminechloridocyanonitritocobalt(III)	$[CoCl(CN)(NH_3)_3(NO_2)]$
	$\left[Zn(NCS)_4\right]^{2^+}$
	$[Cd(SCN)_4]^{2+}$
Lithium tetrahydridoaluminate(III)	Li[AlH <sub>4</sub> ]
Potassium amminetricyanooxoperoxochromate (V)	$K_2^{+2}[Cr^{+5}(CN^{-3})_3O^{-2}(O_2)^{-2}NH_3]^{-2}$
Potassium amminetricyanooxosuperoxochromate (IV)	$K_2^{+2}[Cr^{+4}(CN^{-3})_3O^{-2}(O_2)^{-1}NH_3]^{-2}$
Calcium oxoperoxosuperoxotriaquachromate (III)	$Ca^{+2}[Cr^{+3}(H_2O^0)_3O^{-2}(O_2)^{-2}(O_2)^{-1}]^{-2}$
Potassium oxodisuperoxotriaquachromate (III)	$K^{+1}[Cr^{+3}(H_2O^0)_3O^{-2}(O_2)_2^{-1\times 2}]^{-1}$
Aluminium oxodisuperoxo triaqua chromate (III)	$AI^{+3}[Cr^{+3}(H_2O^0)_3O^{-2}(O_2)_2^{-2\times 2}]^{-3}$
Bis (cyclopentadienyl) iron (II)	$[Fe(C_5H_5)_2]$
Dibenzene chromium (0)	$[\operatorname{Cr}(\operatorname{C}_6\operatorname{H}_6)_2]$
Ammonium heptafluoridozirconate(IV)	$(NH_4)_3$ [ZrF <sub>7</sub> ]
Tetraaquadibromoidochromium(III) chloride	$[Cr(H_2O)_4Br_2]Cl$
	Potassium amminetricyanooxoperoxochromate (V)  Potassium amminetricyanooxosuperoxochromate (IV)  Calcium oxoperoxosuperoxotriaquachromate (III)  Potassium oxodisuperoxotriaquachromate (III)  Aluminium oxodisuperoxotriaquachromate (III)  Bis (cyclopentadienyl) iron (II)  Dibenzene chromium (0)  Ammonium heptafluoridozirconate(IV)

#### ILLUSTRATION 7.6

Write the formula for the following coordination compounds.

- I. a. Tetraamineaquachlorido cobalt (III) chloride
  - b. Potassium tetrahydroxozincate (II)
  - c. Potassium trioxalatoaluminate (III)
  - d. Dichloridobis (ethane-1, 2-diamine)cobalt(III) ion
  - e. Tetracarbonylnickel(0)
- II. Write the IUPAC names of the following coordination compounds.
  - a.  $[Pt(NH_3)_2Cl(NO_2)]$
- b.  $K_3[Cr(C_2O_4)_3]$
- c. [CoCl2(en)2]Cl
- d. [Co(NH<sub>2</sub>)<sub>5</sub>(CO<sub>2</sub>)]Cl
- e. Hg[Co(SCN)<sub>4</sub>]
- Sol. I. a.  $[Co(NH_3)_4(H_2O)Cl]Cl_3$ 
  - b.  $K_2[Zn(OH)_4]$
- c.  $K_3[Al(C_2O_4)_3]$
- d.  $[CoCl_2(en)_2]^{\oplus}$
- e. [Ni(CO)<sub>4</sub>]
- II. a. Diamminechloridonitrito-N-platinum(II)
  - b. Potassium trioxalatochromate(III)
  - c. Dichloridobis (ethane-1, 2-diamine) cobalt(III) chloride
  - d. Pentaamminecarbonatocobalt(III) chloride
  - e. Mercury tetrathiocyanatocobaltate(III)

### ILLUSTRATION 7.7

Write the formula for the following coor-dination compounds.

- Tetrahydroxozincate(II) ion
- Pentaaquachloridochromium(II) chloride
- Tetrabromidocuprate(II) ion
- **d.** Pentacarbonyl iron(0)

- Potassium tetracyanocuprate(II)
- Tetraamminediaquanickel(II) sulphate
- Tetraaquadichloridoiron (III) ion
- Potassium trioxalatochromate (III)
- Pentachloridoazidoosmiate(IV) ion
- Triaquachloridoplatinum(II) bromide.
- **Sol. a.**  $[Z_n^{+2}(OH_{4}^{-4})_4]^{2-}$  **b.**  $[C_n^{+2}Cl(H_2O)_5^0]Cl^{-1}$  **c.**  $[CuBr_4^{-4}]^{2-}$  **d.**  $[Fe(CO)_5]$

- **e.**  $K_2[Cu(CN)_4]$  **f.**  $[Ni(H_2O)_2(NH_3^0)_4](SO_4)^{-2}$
- **g.**  $[Fe Cl_2^{-2}(H_2O)_4]^{\oplus}$  **h.**  $K_3^{+3}[Cr(C_2O_4)_3]^{-3}$  **i.**  $[Os Cl_5^{-5}(N_3)^{-1}]^{2-}$  **j.**  $[Pt Cl(H_2O)_3]Br$

#### ILLUSTRATION 7.8

Name the following complex ions:

- a.  $[PdBr_A]^{2-}$
- **b.**  $[CuCl_2]^{\Theta}$
- c.  $[Au(CN)_4]^{\Theta}$
- **d.**  $[AlF_6]^{3-}$
- e.  $[Cr(NH_3)_6]^{3+}$
- f.  $[Zn(NH_3)_4]^{2+}$
- g. [Fe(CN)<sub>6</sub>]<sup>3</sup>
- a. Tetrabromidopalladate(II) ion
  - b. Dichloridocuprate(I) ion
  - c. Tetracyanoaurate(III) ion
  - d. Hexafluoridoaluminate(III) ion
  - Hexaamminechromium(III) ion
  - Tetraamminezincate(II) ion
  - Hexacyanoferrate(III) ion

# 1.6 WERNER'S COORDINATION **THEORY**

Werner is known as father of coordination chemistry. Affice 's coordination theory (in 1893) was the first attempt to plain the bonding in the coordination complexes. This theory and expansion and the state of the Nobel Prize in chemistry in 1913.

The chief methods available to Werner for the investi-gation of complexes were the study of chemical reactivity, electrical onductivity and isomerism. The following example, taken from his work illustrate their applications by the action of oxidising grents on solution of cobalt (II) chloride in the presence of aminonia the following compounds are formed.

S. No.	Compound	No. of chloride ions precipitated by AgNO <sub>3</sub>	Molar conduc- tivity	Cryoscopic studies
1.	CoCl <sub>3</sub> ·6NH <sub>3</sub> Leutiocobaltic chloride (yellow)	3	6 charges	4 particles
2.	CoCl <sub>3</sub> ·5NH <sub>3</sub> ·H <sub>2</sub> O Roseocobaltic chloride (Red)	3	6 charges	4 particles
3.	CoCl <sub>3</sub> ·5NH <sub>3</sub> Purpureocobaltic chloride (Purple)	2	4 charges	3 particles
4.	CoCl <sub>3</sub> ·4NH <sub>3</sub> Violeocobaltic chloride (Violet)	1	2 charges	2 particles
5.	CoCl <sub>3</sub> -4NH <sub>3</sub> Paraseocobaltic chloride (Green)	1	2 charges	2 particles

#### 7.6.1 Main Postulates of Werner's Theory

 $\ensuremath{\mathbb{T}_0}$  explain the above observations, Werner proposed Werner's coordination theory. Its postulates are:

- 1. A metal possesses two types of valencies:
  - a. Primary or ionisable valency (.....)
  - **b.** Secondary or non-ionisable valency (—
- 2. Characteristics of primary or ionisable valency:
  - i. It corresponds to the oxidation state of the metal atom/ ion or charge carried by the metal ion in the compound.
  - ii. Primary valence of the metal ion is neutralised and satisfied by negative ion such as  $Cl^{\Theta}$ ,  $SO_4^{2-}$  etc.
  - iii. The attachment of metal ion with the negative ligand is shown by dotted lines (- - - -).
- 3. Characteristics of secondary or non-ionisable valency:
  - This corresponds to the coordination number of the metal atom or ion.
  - Secondary valencies may be satisfied by either negative ions or neutral molecules.

- iii. Ligands are directly attached to the metal atom/ion by secondary valency and are shown by thick line (----).
- iv. In modern terms, while writing the structure of a complex species satisfying the secondary valence and metal are written inside the coordination sphere (represented by
- v. Secondary valencies are directional in character, since the species satisfying the secondary valency (i.e. ligands) are directed towards the fixed position in space, which gives rise to characteristic spatial arrangement corresponding to different coordination numbers. Such spatial arrangements are called coordination polyhedra.

Werner observed that every element must satisfy all its primary and secondary valencies.

In order to meet this requirement the negative ion may have a dual behaviour, i.e., in satisfying the primary valency and in satisfying the secondary valency. Further the ligands which satisfying the secondary valencies must point out in definite directions in space whereas the primary valencies are non-directional in nature. Thus the presence of secondary valencies attribute to the isomerism in inorganic complexes, i.e., stereoisomerism.

Thus on the basis of Werner theory CoCl<sub>3</sub>·6NH<sub>3</sub> is called hexammine cobalt (III) chloride because there are six ammonia ligands and the cobalt is in the +3 oxidation state, i.e. cobalt has three primary valencies and six secondary valencies.

Similarly, other complexes of cobalt and ammonia such as CoCl<sub>3</sub>·5NH<sub>3</sub>, CoCl<sub>3</sub>·4NH<sub>3</sub> and CoCl<sub>3</sub>·3NH<sub>3</sub> can be represented as follows.

It is clear from the above formulae that complex compound (as given by Werner), has one characteristic feature, i.e., some of the negative ligands such as chlorine has to perform two functions in satisfying both the primary and secondary valencies and is shown to be attached to the metal ion by dotted and thick lines. Such valencies which perform a dual role are not ionised.

Thus the above compounds will have varying number of ionisable chlorine atoms which is represented as below:

Compound	No. of ionisable chlorine atoms
CoCl <sub>3</sub> ·6NH <sub>3</sub>	3
CoCl <sub>3</sub> ·5NH <sub>3</sub>	2
CoCl <sub>3</sub> ·4NH <sub>3</sub>	1
CoCl <sub>3</sub> ·3NH <sub>3</sub>	Nil

In modern terms the complex ions are shown in square brackets with ionisable ligands outside the coordination sphere. The primary valencies are ionic bonds whereas secondary valencies are coordinate bonds. Thus the above complex can be rewritten in modern terms as below:

Werner formula	Modern formula	Cation	Anion	Total no. of ions
CoCl <sub>3</sub> ·6NH <sub>3</sub>	[Co(NH <sub>3</sub> ) <sub>6</sub> ]Cl <sub>3</sub>	$[Co(NH_3)_6]^{3+}$	3Cl <sup>⊖</sup>	4
CoCl <sub>3</sub> ·5NH <sub>3</sub>	[Co(NH <sub>3</sub> ) <sub>5</sub> Cl]Cl <sub>2</sub>	[Co(NH <sub>3</sub> ) <sub>5</sub> Cl] <sup>2+</sup>	2Cl <sup>⊖</sup>	3
CoCl <sub>3</sub> -4NH <sub>3</sub>	[Co(NH <sub>3</sub> ) <sub>4</sub> Cl <sub>2</sub> ]Cl	$[\text{Co(NH}_3)_4\text{Cl}_2]^{\oplus}$	Cl <sup>⊖</sup>	2
CoCl <sub>3</sub> ·3NH <sub>3</sub>	[Co(NH <sub>3</sub> ) <sub>3</sub> Cl <sub>3</sub> ]	Non-electrolyte	_	zero

#### 7.6.2 FAILURE OF WERNER'S THEORY

Werner was the first to describe the bonding features in coordination compounds. But his theory could not answer basic questions like:

- i. Why only certain elements possess the remarkable property of forming coordination compounds?
- ii. Why the bonds in coordination compounds have direction properties?
- iii. Why coordination compounds have characteristic magnetic and optical properties?

Many approaches have been put forth to explain the nature of bonding in coordination compounds viz. valence theory (VBT), crystal field theory (CFT), ligand field theory (LFT) and molecular orbital theory (MOT). However, we shall be restricting ourselves to VBT and CFT only.

#### ILLUSTRATION 7.9

From the experimental facts given below determine the correct structure of solid CrCl<sub>3</sub>·6H<sub>2</sub>O. Solution containing 0.2665 g of CrCl<sub>3</sub>·6H<sub>2</sub>O was passed through cation exchange resin in acid form. The acid liberated was found to react completely with 30 mL of 0.10 M NaOH. (Molecular mass of  $CrCl_3 \cdot 6H_2O = 266.5$ )

**Sol. d.** Moles of compound = 
$$\frac{0.2665}{266.5} = 10^{-3}$$
 moles

Moles of NaOH = 
$$\frac{30 \text{ mL} \times 0.10 \text{ M}}{1000 \text{ mL}} = 3 \times 10^{-3}$$

Moles of NaOH = Moles of HCl =  $3 \times 10^{-3}$ 

Let 1 mole of compound contains n moles of replaceable  $Cl^{\circ}$ ions.

∴  $10^{-3}$  moles of compound contains =  $n \times 10^{-3}$  moles of Cio

$$n \times 10^{-3} = 3 \times 10^{-3}$$

Therefore, there are 3 moles of replaceable  $Cl^{\ominus}$  in the compound So, CrCl<sub>3</sub>·6H<sub>2</sub>O is represented as [Cr(H<sub>2</sub>O)<sub>6</sub>]Cl<sub>3</sub>.

#### ILLUSTRATION 7.10

Which of the following complexes (in solution) will have greater value of molar conductivity? Explain giving reason,

- a.  $K_4[Fe(CN)_6]$  and  $K_3[Fe(CN)_6]$
- **b**.  $[Pt(NH_3)_2Cl_2]$  and  $[Pt(NH_3)_6]Cl_4$

#### Sol.

a. On ionisation, K<sub>4</sub>[Fe(CN)<sub>6</sub>] gives

$$K_4[Fe(CN)_6] \longrightarrow \underbrace{4K^{\oplus} + [Fe(CN)_6]^4}_{five ions}$$

Whereas K<sub>3</sub>[Fe(CN)<sub>6</sub>] on ionisation gives

$$K_3[Fe(CN)_6] \longrightarrow \underbrace{3K^{\oplus} + [Fe(CN)_6]^{3-}}_{four ions}$$

Since  $K_4[Fe(CN)_6]$  gives more number of ions (i.e. five ions) as compared to K<sub>3</sub>[Fe(CN)<sub>6</sub>], (i.e. four ions) on ionisation.  $K_4[Fe(CN)_6]$  will have greater value of molar conductivity.

b. [Pt(NH<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>] is a non-electrolyte, it does not ionise in solution whereas [Pt(NH<sub>3</sub>)<sub>6</sub>]Cl<sub>4</sub> ionises to give

$$[Pt(NH_3)_6]Cl_4 \longrightarrow \underbrace{[Pt(NH_3)_6]^{4+} + 4 Cl^{\odot}}_{five ions}$$

Hence [Pt(NH3)6]Cl4 will have greater molar conductivity as compared to [Pt(NH<sub>2</sub>)<sub>2</sub>Cl<sub>2</sub>].

#### ILLUSTRATION 7.11

Arrange the following in order of increasing molar conductivity:

- **a.**  $K[Co(NH_3)_2(NO_2)_4]$
- **b.**  $[Cr(NH_3)_3(NO_2)_3]$
- c.  $[Cr(NH_3)_5(NO_2)]_3 [Co(NO_2)_6]_2$
- **d.**  $Mg[Co(NH_3)(NO_2)_5]$

Sol. In aqueous solution

**a.**  $K[Co(NH_3)_2(NO_2)_4]$ 

$$\underbrace{\text{on ionisation}}_{\text{2 jons: charge = +1 or -l}} \underbrace{\left[K^{\oplus} + \left[\text{Co(NH}_3)_2(\text{NO}_2)_{\downarrow}\right]^{\ominus}\right]}_{\text{2 jons: charge = +1 or -l}}$$

- **b.**  $[Cr(NH_3)_3(NO_2)_3]$  being non-electrolyte, does not ionise.
- **c.**  $[Cr(NH_3)_5(NO_2)]_3 [Co(NO_2)_6]_2$

on ionisation
$$3[Cr(NH_3)_5(NO_2)]^{2+} + 2[Co(NO_2)_6]^{3}$$
5 ions; charge = +6 or -6

**d.**  $Mg[Cr(NH_3)(NO_2)_5]$ 

on ionisation 
$$Mg^{2+} + [Cr^{3+}(NH_3^0)(NO_2^{-5})_5]^{-2}$$
  
2 ions; charge = +2 or -2

Greater the number of ions and greater the total (positive or graphic) charge produced after ionisation, greater is the value of graphic conductivity. Hence, increasing order of molar conductivity and conducti

# ILLUSTRATION 7.12

Amange the following in order of decreasing molar conductivity maqueous solution:

- 1 Li[Co(NH<sub>3</sub>)<sub>2</sub>(NO<sub>2</sub>)<sub>4</sub>]
- h Na[Co(NH<sub>3</sub>)<sub>2</sub>(NO<sub>2</sub>)<sub>4</sub>]
- 6. K[Co(NH<sub>3</sub>)<sub>2</sub>(NO<sub>2</sub>)<sub>4</sub>]
- d Cs[Co(NH<sub>3</sub>)<sub>2</sub> (NO<sub>2</sub>)<sub>4</sub>]

The above mentioned complexes ionises as follows:

$$\mathbf{a.} \operatorname{Li[Co(NH_3)_2(NO_2)_4]} \longrightarrow \operatorname{Li_{(aq)}^{\oplus}} + [\operatorname{Co(NH_3)_2(NO_2)_4}]_{(aq)}^{\ominus}$$

$$\text{h. Na}[\text{Co(NH}_3)_2(\text{NO}_2)_4] \longrightarrow \text{Na}_{(\text{aq})}^{\oplus} + [\text{Co(NH}_3)_2(\text{NO}_2)_4]_{(\text{aq})}^{\ominus}$$

$$_{\mathfrak{c}.} \ K[\text{Co(NH}_3)_2(\text{NO}_2)_4] \longrightarrow K_{(\text{aq})}^{\oplus} + [\text{Co(NH}_3)_2(\text{NO}_2)_4]_{(\text{aq})}^{\ominus}$$

$$\text{d. } \mathsf{Cs}[\mathsf{Co}(\mathsf{NH}_3)_2(\mathsf{NO}_2)_4] \longrightarrow \mathsf{Cs}^{\oplus}_{(\mathsf{aq})} + [\mathsf{Co}(\mathsf{NH}_3)_2(\mathsf{NO}_2)_4]^{\ominus}_{(\mathsf{aq})}$$

In all the cases, the number of ionic species produced are same (two in each case), the number of charges produced are same (+1 or -1). Molar conductivity depends directly on the mobility or movement of species produced on ionisation. Mobility of ions  $\infty$  charge density.

Since the charge density (ionic charge/ionic radius) decreases and hence the mobilities of ions should be in the order as:

$$Li^{\oplus} > Na^{\oplus} > K^{\oplus} > Cs^{\oplus}$$

But in aqueous solution, the above order of mobilities is reversed, because hydration  $\infty$  charge density  $\infty$  mobilities. So  $\operatorname{Li}^{\oplus}$  ion is extensively hydrated than  $\operatorname{Cs}^{\oplus}$  ion and hence the mobilities and conductance of the above compounds is in the order d > c > b > a.

# 7.7 SIDGWICK'S ELECTRONIC CONCEPT OF COORDINATE BOND

In 1927, Sidgwick introduced the concept of coordinate bond, which is also sometimes called polar or dative bond. According to Sidgwick, a ligand donates an electron pair to the central metal ion and thus a coordinate bond is formed, which is designated as L→M. This concept is based on the fact that all the ligands contain at least one lone pair of electrons.

# 7.7.1 SIDGWICK'S EFFECTIVE ATOMIC NUMBER (EAN) RULE

On the basis of his concept of coordinate bond, Sidgwick suggested that central metal ion will continue accepting electron pairs from the ligands till the total number of electron surrounding the metal ion including those donated by the ligands is equal to that of next noble gas. The total number of electrons is called **Effective Atomic Number** and the rule is known as Effective Atomic Number (EAN) rule.

Effective atomic number of central atom/ion in the complex can be calculated as follows:

$$EAN = Z - X + Y$$

Z = Atomic number of central atom/ion

X = Oxidation state of central atom/ion

Y = No. of electrons gained by L $\rightarrow$ M coordination

Table 7.12 Complexes whose central atom/ion obeys EAN rule

Complex	Central atom	Atomic Number (Z)	Oxidation state of central atom (X)	Electrons gained by coordination (Y)	EAN (= Z - X + Y)	Atomic number of next higher noble gas
FOCAT 14	Ea	26	+ 2	$2 \times 6 = 12$	26 - 2 + 12 = 36	Kr = 36
[Fe(CN) <sub>6</sub> ] <sup>4</sup>	Fe		+ 1	$2 \times 4 = 8$	29 - 1 + 8 = 36	Kr = 36
$[Cu(CN)_4]^{3-}$	Cu	29		_	46 - 4 + 12 = 54	Xe = 54
$[Pd(NH_3)_6]^{4+}$	Pd	46	+ 4	$2\times 6=12$		
$[PdCl_{4}]^{2-}$	Pd	46	+ 2	$2\times 4=8$	46 - 2 + 8 = 54	Xe = 54
$[Pt(NH_3)_4]^{2+}$	Pt	78	+ 2	$2 \times 4 = 8$	78 - 2 + 8 = 84	Rn = 86
[Cr(CO) <sub>6</sub> ]	Cr	24	0	$2 \times 6 = 12$	24 - 0 + 12 = 36	Kr = 36
			0	$2 \times 5 = 10$	26 - 0 + 10 = 36	Kr = 36
[Fe(CO) <sub>5</sub> ]	Fe	26	V			Kr = 36
$[Ni(CO)_4]$	Ni	28	0	$2 \times 4 = 8$	28 - 0 + 8 = 36	KI - 30

EAN rule has some usefulness, that is, it predicts the number of ligands in many complexes. It has, however, only of qualitative significance, because there are many other complexes which are known to be very stable, but do not obey EAN rule, as shown in Table 7 13

Table 7.13 Complex whose central atom does not obeys EAN rule

Complex	Central atom	Atomic number (Z)	Oxidation state (X)	Electrons gained by coordination (Y)	EAN (= Z - X + Y)
FF (CN) 13-	Fe	26	+ 3	$2 \times 6 = 12$	26 - 3 + 12 = 35
[Fe(CN) <sub>6</sub> ] <sup>3-</sup>	Cr	24	+ 3	$2 \times 6 = 12$	24 - 3 + 12 = 33
$[Cr(NH_3)_6]^{3+}$ $[Ni(NH_3)_6]^{2+}$	Ni	28	+ 2	$2 \times 6 = 12$	28 - 2 + 12 = 38
	Ni	28	+ 2	$*2 \times 3 \times 2 = 12$	28 - 2 + 12 = 38
$[Ni(en)_3]^{2+}$	Mn	25	+ 2	$2 \times 6 = 12$	25 - 2 + 12 = 35
$[Mn(H_2O)_6]^{2+}$	Co	27	+ 2	$2 \times 6 = 12$	27 - 2 + 12 = 37
$[C_0(CN)_6]^{4-}$	Cu	29	· + 2	$2 \times 4 = 8$	29 - 2 + 8 = 35
$[Cu(NH_3)_4]^{2+}$ $[Ni(CN)_4]^{2-}$	Ni	28	+ 2	$2 \times 4 = 8$	28 - 2 + 8 = 34
[M(CN)4]	INI	20			37

\*Note: (en) is bidentate ligand.

#### 7.7.2 APPLICATIONS OF EAN RULE

- 1. It predicts the number of unpaired electrons in the complex and hence magnetic moment.
- 2. It predicts the molecular formula of simple carbonyl.

#### ILLUSTRATION 7.13

Calculate the EAN of the underlined atoms in the following complexes.

- a.  $[Ca(edta)]^{2-}$
- b.  $[Ni (py) (en) (NH_3)_3]^{2+}$

**a.**  $[Ca(edta)]^{2-1}$ 

(Z of Ca = 20)

Let oxidation state of Ca be x,

$$\therefore x+1\times(-4)=-2$$

$$\Rightarrow x = +2$$

Coordination number of (edta) = 6.

(: edta4 is hexadentate ligand)

: EAN of Ca = 
$$(20-2) + 2 \times 6 = 30$$

So, EAN rule is not valid.

**b.**  $[Ni (py) (en) (NH_3)_3]^{2+}$ 

Ni 
$$(Z = 28)$$
:

Let oxidation state of Ni be x,

$$\therefore x + 0 + 0 + 3 \times 0 = 2$$

$$\Rightarrow x = +2$$

[Pyridine, (py); and ammonia, (NH3) are monoden-tate ligand whereas ethylenediamine (en) is bidentate ligand] So, EAN of Ni =  $(28-2) + 2 + 2 + 2 \times 3 = 38$ 

So, EAN rule is not valid.

### ILLUSTRATION 7.14

Deduce the value of x in the following compounds.

- a. [Mo(CO),]
- **b.**  $[Co_2(CO)_v]$
- c.  $H_rCr(CO)_5$
- **d.**  $H_rCo(CO)_4$
- e.  $[Fe(C_5H_5)_2]$
- **f.**  $[Cr(C_6H_6)_2]$

a. In  $[Mo(CO)_r]$ , EAN of Mo = 54

$$Z \text{ of } Mo = 42$$

Oxidation state of Mo is zero

No. of electrons donated by x CO groups = 2x

EAN of Mo in [Mo(CO)x]

$$42 - 0 + 2x = 54$$

$$\therefore x = \frac{54 - 42}{2} = 6$$

Formula is  $[Mo(CO)_6]$ .

**b.**  $[Co_2(CO)_y];$ 

Atomic number (Z) of Co = 27

Oxidation state of  $C_0 = 0$ 

In [Co<sub>2</sub>(CO)<sub>1</sub>], i.e. one electron is shared with other Co atom due to Co-Co bond, which means contribution coming because of Co-Co bond is 1.

For EAN of each Co = 36,

$$27 - 0 + 1 + \frac{2x}{2} = 36$$

$$\Rightarrow x = 8$$

Formula is Co<sub>2</sub>(CO)<sub>8</sub>

c.  $H_xCr(CO)_5$ 

Atomic number (Z) of Cr = 24

Electrons gained by 5 CO groups =  $2 \times 5 = 10$ 

EAN of Cr = 36 = 24 + 10 + x

$$\Rightarrow x = 36 - 24 - 10 = 2$$

i.e, formula is H<sub>2</sub>Cr(CO)<sub>5</sub>.

**d.**  $H_x$ Co(CO)<sub>4</sub>

Atomic number (Z) of Co = 27

Electrons gained by Co due to 4 CO groups =  $2 \times 4 = 8$ 

EAN of 
$$Co = 36 = 27 + 8 + x$$

$$\Rightarrow x = 36 - 27 - 8 = 1$$

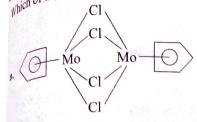
i.e. formula is  $HCo(CO)_4$ .

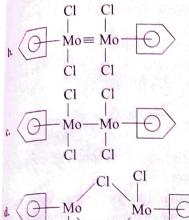
**e.** EAN = 36 **f.** EAN = 36

Refer to Section 7.16.1(b), Point 2, Figs. 7.50 and 7.51.

# USTRATION 7.15

which of the following follow EAN rule.





## Sol.

a. 1st method: Neutral metal  $e^-$  count method.

$$2M_0 = 42 \times 2 = 84e^{-3}$$
's

$$(Mo - Mo)$$
 bond =  $2e^{-1}$ 's

(Bridging halogens) = Each halogen  $e^-$  donor

$$= 3 \times 4$$
 (C1)  $= 12e^{-3}$ 's

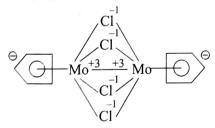
 $2(\text{Cyclopentadiene}) = 2 \times 5e^{-} = 10$ 

$$\therefore EAN = 84 + 2 + 12 + 10 = \frac{108}{18} = 6$$

EAN should be 18 or multiple 18.

Hence if follows EAN rule.

**2nd Method:** Oxidation state  $e^-$  count method:



$$Mo^{+3} = (42 - 2) = 39$$

$$2\text{Mo}^{+3} = 39 \times 2 = 78e^{-3}$$

$$(Mo - Mo)$$
 bond =  $2e^{-1}$ 's

(Bridging halide) = Each halogen  $4e^-$  donor

$$= 4 \times 4$$
 (Cl)  $= 16e^{-3}$ 's

 $2(Cylopentadienyl anion) = 2 \times 6e^- = 12e^-$ 's

$$\therefore$$
 EAN = 78 + 2 + 16 + 12 =  $\frac{108}{18}$  = 6

Hence it follows EAN rule.

## b. 1st Method: Neutral metal e count method:

$$2\text{Mo} = 42 \times 2 = 84e^{-3}$$
s

$$(Mo = Mo) = 2 \times 3 = 6e^{-3}$$

$$4(Single bonded halogens) = 1e^- donor$$

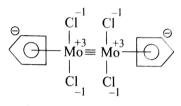
$$= 4 \times 1 = 4e^{-}$$

$$2(\text{Cyclopentadiene}) = 2 \times 5e^- = 10e^-$$

$$\therefore$$
 EAN = 84 + 6 + 4 + 10 = 104 (Not multiple of 18)

Hence does not follow EAN rule.

#### 2nd Method: Oxidation state $e^-$ count method:



$$2\text{Mo}^{+3} = 2(42 - 3) = 39 \times 2 = 78$$

$$(Mo \equiv Mo) bond = 2 \times 3 = 6$$

4(Single bonded halogen) = Each halogen 2e<sup>-</sup> donor

$$= 2 \times 4 = 8e^{-}$$

 $2(Cyclopentadienyl anion) = 2 \times 4 = 8e^{-}$ 

 $2(Cyclopentadienyl anion) = 2 \times 6 = 12e^{-}$ 

 $\therefore$  EAN = 78 + 6 + 8 + 12 = 104 (Not multiple of 18)

Hence does not follow EAN rule.

#### c. 1st Method: Neutral metal e count method:

$$2\text{Mo} = 42 \times 2 = 84e^{-}$$

$$(Mo - Mo) bond = 2e^{-}$$

 $4(Single bonded halogens) = 1e^- donor$ 

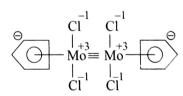
$$= 4 \times 1 = 4e^{-}$$

 $2(Cyclopentadiene) = 2 \times 10 = 10e^{-}$ 

EAN = 84 + 2 + 4 + 10 = 100 (Not multiple of 18).

Hence does not follow EAN rule.

#### 2nd Method: Oxidation state $e^-$ count method:



$$2(Mo^{+3}) = (42 - 3) = 39 \times 2 = 78$$

$$(Mo - Mo)$$
 bond =  $2e^{-}$ 

 $4(Single bonded halogens) = 2e^-donor$ 

$$= 4 \times 2 = 8e^{-}$$

 $2(Cyclopentadienyl anion) = 2 \times 6 = 12e^{-}$ 

 $\therefore$  EAN = 78 + 2 + 8 + 12 = 100 (Not multiple of 18).

Hence does not follow EAN rule.

### d. 1st Method: Neutral metal e count method:

$$2Mo = 42 \times 2 = 84e^{-}$$

$$(Mo - Mo)$$
 bond =  $2e^{-}$ 

2(Bridging halogens) = Each halogen  $3e^-$  donor

$$= 3 \times 2 = 6e^{-}$$

2(Single bonded halogens) = Each halogen 
$$4e^-$$
 donor  
=  $1 \times 2 = 2e^-$ 

 $2(Cyclopentadiene) = 2 \times 5 = 10e^{-}$ 

 $\therefore$  EAN = 84 + 2 + 6 + 2 + 10 = 104 (Not multiple of 18). Hence does not follow EAN rule.

2nd Method: Oxidation state  $e^-$  count method:

$$2(Mo^{+3}) = 2(42 - 3) = 39 \times 2 = 78e^{-3}$$

$$(Mo - Mo) bond = 2e^{-}$$

2(Single bonded halogens) = Each halogen 
$$2e^-$$
 donor  
=  $2 \times 2 = 4e^-$ 

2(Bridging halogens) = Each halogen 
$$4e^-$$
 donor  
=  $2 \times 4 = 8e^-$ 

$$2(Cyclopentadienyl anion) = 2 \times 6 = 12e^{-}$$

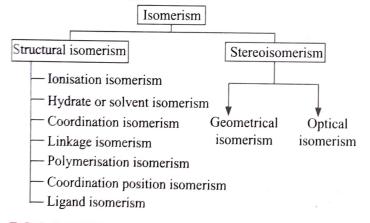
$$\therefore$$
 EAN = 78 + 2 + 4 + 8 + 12 = 104 (Not multiple of 18). Hence does not follow EAN rule.

# 7.8 ISOMERISM IN COORDINATION COMPOUNDS

Complexes which have the same molecular or ionic formula, i.e. same chemical composition, but differ in structural arrangement of their atoms are called isomers. These isomers have different properties. The phenomenon that gives rise to different isomers is called isomerism.

Coordination compounds exhibit two main type of isomerism

- A. Structural isomerism
- B. Stereoisomerism



#### 7.8.1 STRUCTURAL ISOMERISM

This isomerism arises in those complexes which have same molecular formula or chemical composition, but differ in structural or atom to atom bonding sequence.

Structural isomerism is of the following types:

1. Ionisation isomerism: Complexes which have the same empirical formula but give different ions in solution or ionisation are called ionisation isomers and the phenomenon is called ionisation isomerism. It arises due to interchange of ligands in the coordination sphere and the ions present outside the coordination sphere. This type of isomerism occurs when the counter ion in a coordination compound

- A.  $[CoBr(NH_3)_5]SO_4$  and  $[Co(NH_3)_5(SO_4)]Br$
- **B.**  $[Co(NO_3)(NH_3)_5]SO_4$  and  $[Co(NH_3)_5(SO_4)]NO_3$
- C.  $[PtCl_2(NH_3)_4]Br_2$  and  $[PtBr_2(NH_3)_4]Cl_3$
- **D.**  $[CrI_2(NH_3)_4]Br$  and  $[CrBrI(NH_3)_4]I$
- a. Qualitative analysis: Ionisation isomers can be distinguished by qualitative analysis. In aqueous medium they ionise to form different ions in solution, e.g.  $[CoBr(NH_3)_5]SO_4$  (A) and  $[Co(NH_3)_5(SO_4)]Br$ (B)(A) gives a white precipitate of BaSO<sub>4</sub> when treated with BaCl<sub>2</sub>, whereas (B) does not give any reaction.  $[CoBr(NH_3)_5]SO_4 \longrightarrow [CoBr(NH_3)_5]_{(aq)}^{2+} + SO_{4(aq)}^{2-}$

$$SO_{4(aq)}^{2-} + BaCl_{2(soln)} \longrightarrow BaSO_4 \downarrow + 2Cl_{(an)}^{\Theta}$$

This indicates that SO<sub>4</sub><sup>2-</sup> is present outside the coordination sphere.

b. With AgNO<sub>3</sub> soluion: (A) does not react with AgNO. soluion but (B) gives pale yellow precipitate. This indicates that Br is present outside the coordination sphere in (II).

$$\begin{split} &[\text{Co(NH}_3)_5(\text{SO}_4)]\text{Br} \longrightarrow [\text{Co(NH}_3)_5(\text{SO}_4)]^{\oplus}_{(\text{aq})} + \text{Br}^{\ominus}_{(\text{aq})} \\ &\text{AgNO}_{3\text{ (Soln)}} + \text{Br}^{\ominus}_{(\text{aq})} \longrightarrow \text{AgBr} \downarrow + \text{NO}^{\ominus}_3 \\ &\text{Pale yellow ppt.} \end{split}$$

c. Conductance method: In aqueous medium, ionisation isomers ionise to give charged species. Greater is the number of ions (particles) or charges produced, greater is the conductance, e.g.

$$[CoBr(NH_3)_5]SO_4(C)$$
 and  $[Co(NH_3)_5SO_4]Br(D)$ 

(C) ionises to give

[CoBr(NH<sub>3</sub>)<sub>5</sub>]SO<sub>4</sub> 
$$\longrightarrow \underbrace{[CoBr(NH_3)_5]^{2^+} + SO_4^{2^-}}_{\text{two ions}}$$

i.e. two ions (or particles) and 4 charges (+2 and -2)

(D) ionises to give

$$[\text{Co(NH}_3)_5\text{SO}_4]\text{Br} \longrightarrow \underbrace{[\text{Co(NH}_3)_5\text{SO}_4]^{\oplus} + \text{Br}^{\ominus}}_{\text{two ions}}$$

i.e. two ions (or particles) and 2 charges (+1 and -1) Since in (C) and (D), number of ions produced are same but (C) has more charges than (D). Thus (C) has more conductivity as compared to (D).

- 2. Hydrate or solvent isomerism: This type of isomerism is similar to ionisation isomerism. Water (H2O) can be present in the complex in two ways:
  - i. as a ligand, i.e. as a part of coordination entity.
  - ii. as water of crystallisation, i.e. outside the coordination

Hydrate isomers are obtained when H<sub>2</sub>O molecule present as water of crystallisation are exchanged by the coordinated groups or ligand present in the coordination entity. Hydrate isomers have different physical and chemical properties.

For example, CrCl<sub>3</sub>·6H<sub>2</sub>O exists in three different isomeric forms:

#### Isomers

#### Colour

a. [CrCl<sub>3</sub>(H<sub>2</sub>O)<sub>3</sub>].3H<sub>2</sub>O

**b.** [CrCl<sub>2</sub>(H<sub>2</sub>O)<sub>4</sub>]Cl·2H<sub>2</sub>O Green

 $\mathfrak{c}$ .  $[CrCl(H_2O)_5]Cl_2 \cdot H_2O$ Bluish green

d.  $[Cr(H_2O)_6]Cl_3$ 

Violet

Apart from their colours, the three isomers can be distinguish by quantitative method by reaction with AgNO<sub>3</sub> in aqueous medium.

a.  $[CrCl_3(H_2O)_3].3H_2O \xrightarrow{aq.} [CrCl_3(H_2O)_3]_{(aq)}$ No precipitation of AgCl.

**b.**  $[CrCl_2(H_2O)_4]Cl\cdot 2H_2O$  $\xrightarrow{\operatorname{aq}} : \left[ \operatorname{CrCl}_{2}(\operatorname{H}_{2}\operatorname{O})_{4} \right]_{(\operatorname{aq})}^{\oplus} + \operatorname{Cl}_{(\operatorname{aq})}^{\ominus}$  $Cl_{(ag)}^{\Theta} + Ag^{\oplus} \longrightarrow AgCl^{\downarrow}$ 

c.  $[CrCl(H_2O)_5]Cl_2 \cdot H_2O$ 

$$\begin{array}{ccc}
&\longrightarrow [\operatorname{CrCl}(H_2O)_5]^{2+} + 2\operatorname{Cl}_{(aq)}^{\Theta} \\
&2\operatorname{Cl}_{(aq)}^{\Theta} + 2\operatorname{Ag}^{\Theta} \longrightarrow 2\operatorname{AgCl}^{\downarrow}
\end{array}$$

d. 
$$[Cr(H_2O)_6]Cl_3 \longrightarrow [Cr(H_2O)_6]^{3+}_{(aq)} + 3Cl_{(aq)}^{\odot}$$

$$3Cl_{(aq)}^{(aq)} + 3Ag^{\oplus} \longrightarrow 3AgCl \downarrow$$

With AgNO<sub>3</sub>, the three isomers (a), (b) and (c) give a white precipitate of AgCl in the molar ratio of 1: 2: 3 respectively, indicating the presence of 1, 2 and 3 moles of  $\mathrm{Cl}^{\odot}$  ions outside the coordination sphere.

These isomers can also be distinguished by conductivity measurement method, which will give different

number of ionic species.

S. No.	Formulae	No. of ionic species	Charges
a.	[CrCl <sub>3</sub> (H <sub>2</sub> O) <sub>3</sub> ].3H <sub>2</sub> O	1	0
b.	[CrCl <sub>2</sub> (H <sub>2</sub> O) <sub>4</sub> ]Cl·2H <sub>2</sub> O	2	2(+1 and -1)
c.	[CrCl(H <sub>2</sub> O) <sub>5</sub> ]Cl <sub>2</sub> ·H <sub>2</sub> O	3	4(+2 and -2)
d.	[Cr(H <sub>2</sub> O) <sub>6</sub> ]Cl <sub>3</sub>	4	6(+3  and  -3)

Since the number of ionic species produced is increasing in the order a < b < c < d, thus molar conductivity also increases in the same order i.e.,  $a \le b \le c \le d$ .

- 3. Coordination isomers: This isomerism is shown by those complexes which are composed of complex cation and complex anion. It arises due to interchange of ligands between the cationic and anionic complex entities. Some of the examples are as follows:
  - **a.**  $[Co(NH_3)_6][Cr(CN)_6]$  is isomeric with [Cr(NH<sub>3</sub>)<sub>6</sub>][Co(CN)<sub>6</sub>]
  - **b.**  $[Cu(NH_3)_4]$  [PtCl<sub>4</sub>] is isomeric with  $[Pt(NH_3)_4][CuCl_4]$
  - c.  $[Cr(NH_3)_6][Cr(SCN)_6]$  is isomeric with  $[Cr(NH_3)_4 (SCN)_2] [Cr(NH_3)_2 (SCN)_4]$

In these pairs the central metal atom in the two coordination spheres may be same or different.

Distinction between coordination isomers:-

Electrolysis methods: Coordination isomers can be distinguished by electrolysis of an aqueous solution. In example (a) above, in first case cobalt complex migrates towards the negative electrode (anode) (: Co complex is positively charged) and Co complex will be deposited at anode.

Cr will be deposited at positive electrode (cathode) since the Cr complex is negatively charged. Reverse will happen in its coordination isomer.

- Conductivity method: In example (c), the former isomer is (+3, -3) electrolyte and latter is (+1, -1)electrolyte), thus conductivity of the former isomer is greater than that of latter.
- iii. These isomers can also be distinguished by X-ray diffraction and IR (infrared) spectroscopic method.
- 4. Linkage isomerism: This type of isomerism is shown by those coordination compounds which contain an ambidentate ligand, e.g.,  $NO_2^{\ominus}$ ,  $SCN^{\ominus}$ ,  $CN^{\ominus}$ ,  $S_2O_3^{2-}$  etc. When an ambidentate ligand, having two different donor atoms coordinates to the central atom through either of its two donor atoms, two different complexes are obtained, and they are known as linkage isomers, the phenomenon is known as linkage isomerism.

For example, [Co(NH<sub>3</sub>)<sub>5</sub>(NO<sub>2</sub>)]Cl<sub>2</sub> and

[Co(NH<sub>3</sub>)<sub>5</sub>(ONO)]Cl<sub>2</sub>. The two linkage isomers are different because they have different structures.  $[Co(NH_3)_5(NO_2)]$  Cl is yellow in colour, whereas [Co(NH<sub>3</sub>)<sub>5</sub>(ONO)]Cl<sub>2</sub> is red in colour.

The two linkage isomers are named as:

 $[\text{Co(NH}_3)_5(\text{NO}_2)]\text{Cl}_2$  pentaamminenitrito-N-cobalt(III)

chloride

 $[Co(NH_3)_5(ONO)]Cl_2$  pentaamminenitrito-O-cobalt(III) chloride

These isomers can be distinguished by UV, IR, NMR spectroscopic and X-ray diffraction methods.

5. Polymerisation isomerism: This type of isomerism exists among those complexes, which have the same empirical formula but each of the isomer is some simple multiple of the empirical formula, e.g.,

Pt:NH<sub>3</sub>:Cl 1:2:2**a. i.**  $[PtCl_2(NH_3)_2]$ 2: 4:4 or 1:2:2 ii.  $[Pt(NH_3)_4][PtCl_4]$ 3: 6:6 or 1:2:2 iii.  $[Pt(NH_3)_3 Cl]_2 [PtCl_4]$ Co:NH<sub>3</sub>: NO<sub>2</sub> 1:3:3 **b.** i.  $[Co(NH_3)_3(NO_2)_3]$ **ii.**  $[Co(NH_3)_6][Co(NO_2)_6]$  2 : 6 : 6 or 1: 3: 3  $[Co(NH_3)_5(NO_2)]_3[Co(NO_2)_6]_2$ 

These isomers can be distinguished by mass spectroscopic methods.

5: 15:15 or 1:3:3

6. Coordination position isomerism: This type of isomerism is shown in polynuclear complexes. This isomerism arises due to interchange of ligands between the coordination sphere of various central metal ion. Coordination position isomerism is thus a special type of coordination isomerism. For example,

a. 
$$\begin{bmatrix} (NH_3)_4 Co & OH \\ OH & Co(NH_3)_2 Cl_2 \end{bmatrix} SO_4 \text{ (Unsymmetrical)}$$

 $- \\ tetra ammine cobalt (III) - di - \mu - hydroxodiam mine chlorido \\ cobalt (III) sulphate$ 

and 
$$Cl(NH_3)_3Co OH Co(NH_3)_3Cl SO_4$$
 (Symmetrical)

triamminechloridocobalt(III)-di-µ-hydroxotriamminechloridocobalt(III) sulphate

**b.** i. 
$$\left[ (NH_3)_4 Co \left( \frac{NH_2}{O_2} \right) Co(NH_3)_2 Cl_2 \right] Cl_2$$
 polynuclear complex)

tetraamminecobalt(III)-μ-amido-μ-peroxodiammine dichloridocobalt(III) chloride

ii. 
$$\left[ NH_3 \right]_3 ClCo \left[ NH_2 \right]_3 Cl \left[ Cl_2 \right]_2 Co(NH_3)_3 Cl \left[ Cl_2 \right]_2 Complex$$
 (Symmetrical polynuclear complex)

 $triammine chlorido cobalt (III)-\mu-amido-\mu-peroxotriammine chlorido cobalt (III) chloride$ 

- or  $\mu$ -amido- $\mu$ -peroxobis(triamminechloridocobalt(III) chloride
- 7. **Ligand isomerism:** This type of isomerism arises because of the ligands, which are present in their isomeric forms, e.g.

Both are bidentate and neutral ligands. When these are coordinated to the metal atom, two isomers are obtained. These are called ligand isomers and the phenomenon is called ligand isomerism.

For example,  $[Co(pn)_2Cl_2]^{\oplus}$  and  $[Co(tn)_2Cl_2]^{\oplus}$ 

$$\begin{bmatrix} H_{3}C & Cl & H_{2} \\ HC-N--\frac{1}{7}--N-CH_{2} \\ \downarrow & Co & \downarrow \\ H_{2}C-N--\frac{1}{7}--N-CH \\ H_{2} & Cl & CH_{3} \end{bmatrix}^{\oplus} \text{ and }$$

$$\begin{bmatrix} H_{2} & CI & H_{2} \\ H_{2}C - N_{1} - - \frac{1}{7} - - N_{2} - CH_{2} \\ H_{2}C & Co \\ H_{2}C - N_{1} - - \frac{1}{7} - - N_{2} - CH_{2} \\ H_{2} & CI \end{bmatrix} \xrightarrow{\text{CH}_{2}} CH_{2}$$

#### ILLUSTRATION 7.16

Describe a simple test to distinguish between the following pairs of compounds:

- i. (A)  $[Co(NH_3)_5Br]SO_4$  and (B)  $[Co(NH_3)_5SO_4]Br$
- ii. (A)  $[Cr(H_2O)_6]Cl_3$  and (B)  $[Cr(H_2O)_5 Cl] Cl_2 \cdot H_2O$
- iii. (A) cis [PtCl<sub>2</sub>(NH<sub>3</sub>)<sub>2</sub>] and (B) trans [PtCl<sub>2</sub>(NH<sub>2</sub>)<sub>2</sub>]
- iv. (A) and (B) Two enantiomers of [Co(en),Cl,1<sup>®</sup>
- v. (A)  $[Cr(NH_3)_6][Cr(NO_2)_6]$  and
  - (B)  $[Cr(NH_3)_4(NO_2)_2][Cr(NH_3)_2(NO_2)_4]$
- vi. (A)  $[Pt(NH_3)_2Cl_2]$  and (B)  $[Pt(NH_3)_6]Cl_2$
- vii. (A) [Co(NH<sub>3</sub>)<sub>5</sub>Cl]SO<sub>4</sub> and (B) [Co(NH<sub>3</sub>)<sub>5</sub>SO<sub>4</sub>] Cl

#### Sol.

- i. (A) and (B) are distinguished by qualitative method. (A) gives white precipitate of BaSO<sub>4</sub> with BaCl<sub>2</sub> solution due to the presence of SO<sub>4</sub><sup>2-</sup> as counter ion. (B) gives pale yellow precipitate of AgBr (partially soluble in NH<sub>4</sub>OH) with AgNO<sub>3</sub> solution due to the presence of Br<sup>©</sup> ion as counter ion.
- ii. (A) and (B) are distinguished by conductance method. (A) gives 4 ions with high charge whereas (B) gives 3 ions with low charge in aqueous solution as shown.

$$A \longrightarrow \underbrace{\left[\text{Cr}(\text{H}_2\text{O})_6\right]^{3^+} + 3\text{Cl}^{\ominus}}_{\text{4 ions (+3 and -3) charge}}$$

$$B \longrightarrow \underbrace{\left[\text{Cr}(\text{H}_2\text{O})_5\text{Cl}\right]^{2^+} + 2\text{Cl}^{\ominus}}_{\text{4 ions (+2 and -2) charge}}$$

So, conductance of (A) will be higher than that of B.

Further (A) and (B) are also distinguished by **quantitative method**, with AgNO<sub>3</sub> (A) and (B) gives a white precipitate of AgCl in the molar ratio of 3: 2 respectively, indicating the presence of 3 and 2 moles of  $Cl^{\Theta}$  as counter ions.

- iii. (A) cis [PtCl<sub>2</sub>(NH<sub>3</sub>)<sub>2</sub>] has some value of dipole moment while the (B) tran [PtCl<sub>2</sub>(NH<sub>3</sub>)<sub>2</sub>] has zero value for its dipole moment.
- iv. One enantiomer of  $[Co(en)_2Cl_2]^{\oplus}$  is dextrorotatory (*d*-form) and the other enantiomer is levorotatory (*l*-form)
- v. The given isomers can be distinguished by conductivity measurement, (A) conducts as (3+, 3-) electrolyte while (B) conducts as (1+, 1-) electrolyte.

(A) 
$$\longrightarrow$$
  $[Cr(NH_3)_6]^{3+} + [Cr(NO_2)_6]^{3-}$   
(3+, 3-) electrolyte

(B) 
$$\longrightarrow$$
  $[Cr(NH_3)_4(NO_2)_2]^{\oplus} + [Cr(NH_3)_2(NO_2)_4]^{\ominus}$   
(1+, 1-) electrolyte

Thus (A) has higher value of molar conductance than (B).

- vi. (A) and (B) can be distinguished by conductance method. The ionisation of the given complex compounds can be shown as
  - $(A) \longrightarrow No ions$

(B) 
$$\longrightarrow \underbrace{[Pt(NH_3)_6]^{3^+} + 2Cl}^{\Theta}$$
 three ions

Therefore (A) has zero value of its electrolytic conductance Thereas (B) gives 3 ions, it has some value of electrolytic whereas (B) gives 3 ions, it has some value of electrolytic

(A) and (B) are distinguished by qualitative method. (A) with B-C! (A) with BaCl<sub>2</sub> solution due gives white prosper of SO<sub>4</sub> ion as counter ion. (B) gives white precipitate of AgCl (soluble in NH<sub>4</sub>OH) with AgNO<sub>3</sub> precipilition due to the presence of Cl<sup>\to</sup> ion as counter ion.

# LUSTRATION 7.17

Write hydrate isomers of the following and also give increasing order of the conductance of the isomers.

 $_{1}$  [Cr(H<sub>2</sub>O)<sub>6</sub>]Br<sub>3</sub>

b. [Cu(H,O),]Cl,

# <sub>a. Hydrate</sub> isomers of [Cr(H<sub>2</sub>O)<sub>6</sub>]Br<sub>3</sub> are:

i. (A)  $[Cr(H_2O)_6]Br_3$ 

ii. (B)  $[Cr(H_2O)_5Br]Br_2 \cdot H_2O$ 

iii. (C)  $[Cr(H_2O)_4Br_2]Br \cdot 2H_2O$ 

iv. (D)  $[Cr(H_2O)_3Br_3] \cdot 3H_2O$ 

On ionisation the above hydrate isomers give

i. (A)  $\leftarrow$   $\left[\operatorname{Cr}(\operatorname{H}_2\operatorname{O})_6\right]^{3+} + 3\operatorname{Br}^{\Theta}(4 \text{ ions})$ 

ii. (B)  $\leftarrow$  [Cr(H<sub>2</sub>O)<sub>5</sub>Br]<sup>2+</sup> + 2Br<sup> $\Theta$ </sup> + H<sub>2</sub>O (3 ions)

iii.  $(C) \leftarrow [Cr(H_2O)_4Br_2]^{\oplus} + Br^{\Theta} + 2H_2O$  (2 ions)

iv. (D) No ions are formed.

Greater the number of ions formed, greater is the conductance. Hence, increasing order of conductance

is D < C < B < A

# b. Hydrate isomers of $[Cu(H_2O)_4]Cl_2$ are

i. (A)  $[Cu(H_2O)_3Cl]Cl\cdot H_2O$ 

ii. (B)  $[Cu(H_2O)_2Cl_2] \cdot 2H_2O$ 

iii. (C)  $[Cu(H_2O)_4]Cl_2$ 

On ionisation, the above hydrate isomers give

i. (A)  $\longrightarrow$  [Cu(H<sub>2</sub>O)<sub>3</sub>Cl]<sup> $\oplus$ </sup> + Cl<sup> $\ominus$ </sup> (2 ions)

ii. (B)  $\longrightarrow$  No ions

iii. (C)  $\longrightarrow$   $[Cu(H_2O)_4]^{2+} + 2Cl^{\Theta}$  (3 ions)

Greater the number of ions formed, greater is the conductance. Hence order of conductance is B < A < C.

# 7.8.2 GEOMETRICAL ISOMERISM

The complex compounds which have the same ligands in the coordination sphere but the relative position of the ligands round the central metal atom is different are called geometrical isomers and the phenomenon is called geometrical isomerism.

In a given complex compound the two ligands may occupy positions either adjacent to each other or opposite to each other. The complex compound having two ligands occupying the adjacent positions to each other is called cis-isomer while that in which the two ligands occupy opposite positions is called transisomer. Hence geometrical isomerism is also called cis-trans isomerism.

Geometrical isomers of a complex differ in physical characteristics such as dipole moment and visible/uv spectra.

# 7.8.2.1 Geometrical Isomerism in Complexes with C.N. 2 and 3

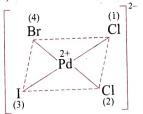
Geometrical isomerism is not found in complex compounds with coordination number 2 and 3, since in these cases all the positions occupied by the ligands round the central metal atom are adjacent to one another.

# 7.8.2.2 Geometrical Isomerism in Tetrahedral Complexes (C.N. = 4)

Geometrical isomerism cannot be shown by tetrahedral complexes, since all the four ligands in this geometry have adjacent position (i.e., cis position) to one another and all the four bond angles are the same (=  $109.5^{\circ}$ ).

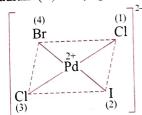
# 7.8.2.3 Geometrical Isomerism in Square Planner Complexes (C.N. = 4)

Before discussing the geometrical isomerism exhibited by various types of square planar complexes, we should know how cis and trans isomers of a square planar complex are named. A square planar complex having similar ligands at adjacent positions (90° apart) is called cis-isomer while a square planar complex having two similar ligands at opposite positions (180° apart) is called trans-isomer. Thus a square planar complex having two similar ligands at 1-2, 2-3, 3-4 and 1-4 positions is called cis-isomer, while that having two similar ligands at 1-3 and 2-4 positions is called trans-isomer, cis-and trans-isomers are also named by numbering system. Thus in [Pd<sup>2+</sup>Cl<sub>2</sub>Br]<sup>2-</sup> if two Cl<sup>©</sup> ions are placed *cis* to each other or at 1-2 positions, it is named as cis-dichloro bromoiodo palladium (II) ion or 1,2-dichloro bromoiodo palladium (II) ion. On the other hand, if two Cl<sup>o</sup> ions are placed trans to each other or at 1-3 positions, it is named as trans-dichlorobromoiodo palladium (II) ion or 1, 3-dichlrobromoiodopalladium (II) ion (Fig. 7.1).



(a) cis-dichloro bromoiodo palladium (II) ion or. 1, 2-dichloro bromoiodo palladium

(II) ion, [Pd<sup>2+</sup>Cl<sub>2</sub>BrI]<sup>2-</sup>



(b) trans-dichloro bromoiodo palladium (II) ion or 1, 3-dichloro bromoiodo palladium (II) ion, [Pd<sup>2+</sup>Cl<sub>2</sub>Brl]<sup>2</sup>

#### Fig. 7.1 Nomenclature of geometrical (cis and trans) isomers of a square planar complex.

Here we shall consider geometrical isomerism in square planar complexes of  $[Ma_4]$ ,  $[Ma_3b]$ ,  $[Mab_3]$ ,  $[Ma_2b_3]$ ,  $[Ma_2bc]$ , [Mabcd]and [M(AB)<sub>2</sub>] type in which M is the central metal atom; a, b, c and d are monodentate ligands and (AB) is an unsymmetrical bidentate ligand, since it has two different donor atoms namely A and B.

1. Square planar complexes of [Ma4], [Ma2b] and [Mab3] type: Square planar complexes of this type do not show geometrical isomerism, since all the possible spatial arrangement of four ligands round the central metal atom is the same.

2. Square planar complexes of [Ma2b2] type. Important examples of square planar complexes of this type are  $[Pt(NH_3)_2(Cl_2)]^0$ ,  $[Pt(py)_2Cl_2]^0$ ,  $[Pd(NH_3)_2(NO_2)_2]^0$  etc. These complexes exist in cis- and trans-isomers. These isomers of  $[Pt^{2+}(NH_3)_2Br_2]^0$  are shown in Fig. 7.2. In (a) since both NH<sub>3</sub> molecules and both Br<sup>©</sup> ions are cis to each other, it is called cis-isomer. On the other hand, in (b) since both  $\mathrm{NH_3}$  molecules and both  $\mathrm{Cl}^\odot$  ions are trans with respect to each other, it is called trans-isomer.

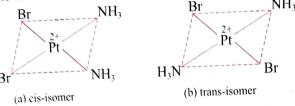


Fig. 7.2 cis- and trans-isomers of  $[Pt^{2+}(NH_3)_2Br_2]^0$ 

3. Square planar complexes of [Mabcd] type. Square planar complexes of this type exist in three isomeric forms. For example, [Pt<sup>2+</sup>(NH<sub>3</sub>)(py)(Cl)(Br)] exists in three isomeric forms shown below in Fig. 7.3. These isomeric forms can be obtained by selecting one ligand, say NH<sub>3</sub>, and then placing the remaining three legands, one by one trans to NH<sub>3</sub>.

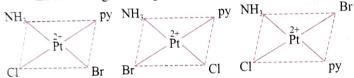


Fig. 7.3 Three isomeric forms of [Pt2+(NH3)(py)(Cl)(Br)]

 $[Pt^{2+}(NO_2)(py)(NH_3)(NH_2OH)]^+$  and  $[Pt^{2+}(C_2H_4)(NH_3)(CI)$ Br] are other examples of square planar complexes which exist in three isomeric forms.

The existence of three isomeric forms in case of the complexes mentioned above indicates that these complexes have square planar geometry.

4. Square planar complexes of [Ma2bc] type. Square planar complexes of this type also show cis-trans isomerism. For example, [Pd<sup>2+</sup>Cl<sub>2</sub>BrI]<sup>2-</sup> ion exists in cis- and trans-isomers as shown below in figure.

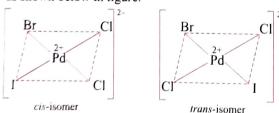


Fig. 7.4 cis- and trans-isomers of [Pd2+Cl2BrI]2- ion

[Pt<sup>2+</sup>(py)<sub>2</sub>(NH<sub>3</sub>)Cl]<sup>-</sup> is another example of square planar complex of [Ma2bc] type which exists in cis- and transisomers.

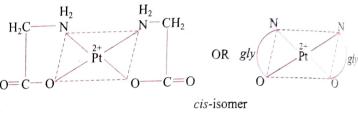
5. Square planar complexes of [M(AB)<sub>2</sub>] type. Here M is the central metal ion and [AB] represents an unsymmetrical bidentate ligand in which A and B are two different coordinating (donor) atoms. Square planar complexes of this type also exist in cis- and trans-isomers. For example,  $[Pt^{2+}(gly)_2]$  exists in *cis*- and *trans*-isomers as shown in Fig. Here gly represents the glycinato ligand, NH<sub>2</sub>.CH<sub>2</sub>COO

which has N and O atoms as its donor atoms (i.e., A = Nand B = O).

 $[Cu^{2+}(gly)_2]^{10}$  is also an example of square planar complex of  $[M(AA)_2]$  type. This complex also exhibits cis-transisomerism.

## 7.8.2.4 Geometrical Isomerism in 6-coordinated **Complexes: Octahedral Complexes**

We know that a complex compound having central atom with coordination number equal to 6 is octahedral in shape. Before discussing the geometrical isomerism exhibited by various types of octahedral complexes, we should know how cis- and trans-isomers of an octahedral complex are named. In an octahedral complex, if two similar ligands are placed on any of the twelve edges of the octahedron, they are said to be in cis position. On the other hand if two similar ligands are lying on a straight line which passes through the center (where the metal ion is placed).



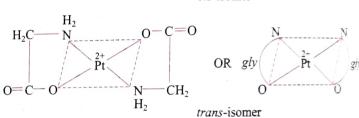


Fig. 7.5 cis- and trans-isomers of [Pt2+(gly),]

they are said to be in trans position. Thus in an octahedral complex, the two ligands at positions 1-6, 2-4 and 3-5 are trans to each other and the two ligands occupying positions 1-2, 1-3, 6-4 etc. are cis to each other.

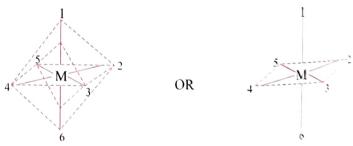


Fig. 7.6 Numbering of six ligands in a regular octahedral complex round the central metal ion, M.

The numbering system of ligands shown in Fig. 7.6 can be exemplified by considering the nomenclature of cis- and transisomers of [Co<sup>3+</sup>(NH<sub>3</sub>)<sub>4</sub>Cl<sub>2</sub>]<sup>+</sup> ion which is an octahedral complex ion. Cis-isomer of this ion in which two CI ions are cis to each other is also called 1, 2-dichlorotetrammine cobalt (III) ion [See Fig. 7.7(a)]. Similarly, *trans*-isomer of this ion in which two Cl ions are trans to each other is also called 1, 6 dichlorotetrammine cobalt (III) ion. [See Fig. 7.7(b)]

Here we shall discuss the geometrical isomerism in octahedral complexes of the following type:

- 1. Octahedral complexes of [Ma<sub>5</sub>] and [Ma<sub>5</sub>b] type: Octahedral complexes of this type do not show geometrical isomerism.
- 2. Octahedral complexes of [Ma<sub>4</sub>b<sub>2</sub>] type: Important examples of octahedral complexes of this type are [Co<sup>3+</sup>(NH<sub>3</sub>)<sub>4</sub>Cl<sub>2</sub>]<sup>+</sup>,  $[C_0^{3+}(NH_3)_4(NO_2)_2]^+$  etc. These complexes exist in *cis*- and trans-isomers. These isomers of  $[Co^{3+}(NH_3)_4Br_3]^{\oplus}$  ion are shown in Fig. 7.7. In cis-isomer two Br ions occupy the adjacent (i.e., 1 and 2) positions of the octahedron while in trans-isomers these ions have the opposite (i.e., 1 and 6) positions. Cis-isomer of [Co<sup>3+</sup>(NH<sub>3</sub>)<sub>4</sub>Br<sub>2</sub>]<sup>©</sup> ion is yellowbrown while trans-form is yellow in colour.
  - (a) cis-isomer, (1, 2-dishlorotetrammine cobalt (III) ion). (yellow-brown)
  - (b) Trans-isomer (1, 6-dishlorotetrammines cobalt (III) ion), (yellow)

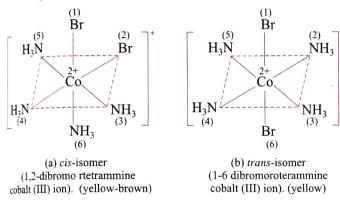


Fig. 7.7 cis- and trans-isomers of [Co3+(NH3)4Br2] ton

- 3. Octahedral complexes of [Ma<sub>3</sub>b<sub>3</sub>] type: We know that an octahedron has eight triangular faces and six corners (vertices). Octahedral complexes of [Ma<sub>3</sub>b<sub>3</sub>] have two types of geometrical isomers:
  - (i) Facial or fac isomer (cis-isomer): In this isomer the three a groups occupy the three corners (vertices) of one triangular face while the other three b groups in this isomer take up the position of the remaining three vertices. This isomer is called facial or fac isomer. This isomer is also called cis isomer, since the three a groups are cis to each other. Similarly b groups are also cis to each other (See Fig. 7.8)

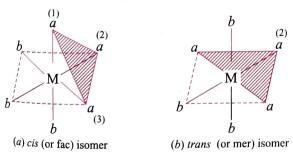


Fig. 7.8 cis- (or fac) and trans (or mer) isomers of  $Ma_3b_3$  type octahedral compléx

(ii) Meridional or mer-isomer (trans-isomer): In this isomer the three a groups are in one plane and the other three b groups are in a perpendicular plane, a and bgroups lie along the meridian of a sphere (imagine our earth). Hence this isomer is called meridional or mer isomer. In this isomer two of the three a groups and also two of the three b groups are trans to each other (See Fig. 7.8). Hence this isomer is also called trans isomer.

**Examples:**  $[Co(NH_3)_3Cl_3]$ ,  $[Co(NH_3)_3(NO_2)_3]$ ,  $[Cr(H_2O)_3F_3][Cr(MH_3)_3Cl_3], [Rh(py)_3Cl_3], [Ru(H_2O)_3Cl_3],$  $[Ir(H_2O)_3Cl_3]$ ,  $[Pt(NH_3)_3Br_3]^+$ ,  $[Pt(NH_3)_3I_3]^+$  etc. are important examples of octahedral complexes of Ma<sub>3</sub>b<sub>3</sub> type. Cis-(fac) and trans-(mer) isomers of [Co(NH<sub>3</sub>)<sub>3</sub>Br<sub>3</sub>] are given in Fig. 7.9.

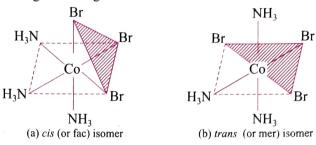
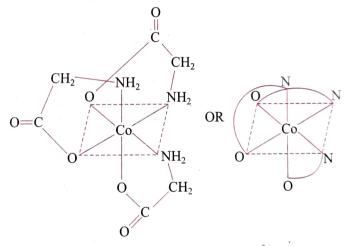
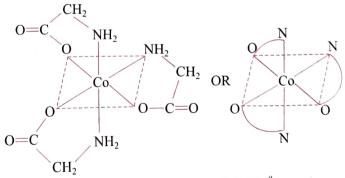


Fig. 7.9 cis (fac) and trans (mer) isomers of [Co(NH<sub>2</sub>)<sub>2</sub>Br<sub>3</sub>] octahedral complex

[Co(NH<sub>2</sub>CH<sub>2</sub>COO)<sub>3</sub>] also has two geometrical isomers, viz., facial and meridional (See Fig. 7.10). In the given complex N and O atoms are the donor atoms.



Facial isomer of [Co(NH,CH,COO)<sub>3</sub>]<sup>0</sup>



Meridional isomer of [Co(NH<sub>2</sub>CH<sub>2</sub>COO)<sub>3</sub>]<sup>0</sup>

Fig. 7.10 Facial and merdional isomers of  $[Co(NH_2CH_2COO)_3]^0$ 

4. Octahedral complexes of [Ma<sub>4</sub>bc] type: [Co<sup>3+</sup>(NH<sub>3</sub>)<sub>4</sub>(H<sub>2</sub>O) Br]<sup>2+</sup> ion is an important example of octahedral complex of [Ma4bc] type. This ion has cis- and trans-isomers whose structures are given in Fig. 7.11. In cis-form two NH<sub>3</sub> molecules have cis positions to each other and in trans-form these ligands (i.e., two NH<sub>3</sub> molecules) have trans positions with each other.

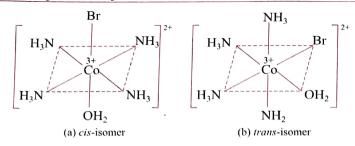


Fig. 7.11 Structure of cis- and trans-isomers of [Co<sup>3+</sup>(NH<sub>3</sub>)<sub>4</sub>(H<sub>2</sub>0)Br]<sup>2+</sup> octahedral complex ion.

5. Octahedral complexes of [Ma<sub>2</sub>b<sub>2</sub>c<sub>2</sub>] type: [Pt<sup>4+</sup>(NH<sub>3</sub>)<sub>2</sub>(py)<sub>2</sub>Br<sub>2</sub>]<sup>2+</sup> ion is an important example of octahedral complex of [Ma<sub>2</sub>b<sub>2</sub>c<sub>2</sub>] type. This ion can exist theoretically in five geometrical isomers that have been shown in Fig. 7.12, but it is only three isomers that have been actually isolated. It may be noted from the figure that (I) form is a cis-form since in this form two identical ligands are occupying adjacent positions. Form (II) is trans-form because in it the two identical ligands are placed at opposite positions.

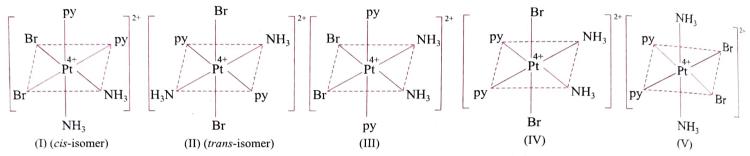


Fig. 7.12 All possible five geometrical isomers of [Pt4+(NH3)2(py)2Br2]2+ ion

- 6. Octahedral complexes of [Mabcdef] type: Octahedral complexes which have different monodentate ligands have been prepared for Pt (IV), [Pt<sup>4+</sup>(py) (NH<sub>3</sub>)(NO<sub>2</sub>)(Cl)(Br)(I)] is the only complex of this type of complexes. Theoretically 15 geometrical isomers are possible for this complex compound. In fact only three geometrical isomers have been isolated.
- 7. Octahedral complexes of M(AA), type: Octahedral complexes of this type of do not show geometrical isomers.
- 8. Octahedral complexes of [M(AA)<sub>2</sub>a<sub>2</sub>] type: Here (AA) represents a symmetrical bidentate ligand in which A and A are two identical coordinating (donor) atoms,  $[Co(en)_2Cl_2]^{\oplus}$ ,  $[Co(en)_2(NH_3)_2]^{3+}$ ,  $[Co(en)_2(NO_3)_2]^{\oplus}$ ,  $[Cr(en)_2Cl_2]^{\oplus}$ ,  $[Cr(C_2O_4)_2(H_2O)_2]^{\oplus}$ ,  $[Cr(C_2O_4)_2(H_2O)_2]^{\oplus}$ ,  $[Cr(C_2O_4)_2Cl_2]^{\oplus}$  and trans-isomers. As an example *cis*-and trans-isomers of  $[Co^{3+}(en)_2Br_2]^{\oplus}$  ion are shown in Fig. 7.13.

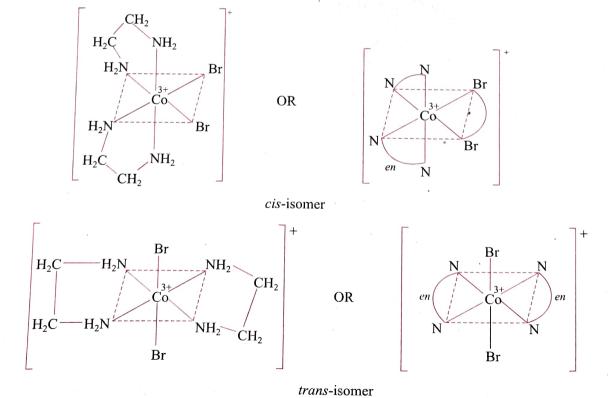
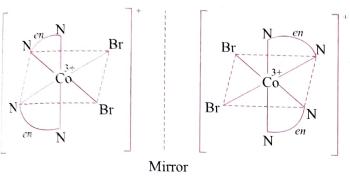
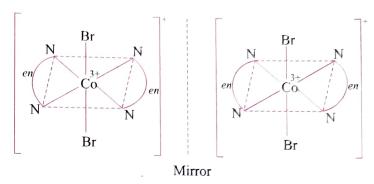


Fig. 7.13 cis- and trans-isomers of [Co3+(en)2Br2]+ on

symmetrical/unsymmetrical nature of cis-and transisomers: The structures of mirror images of cis-and transforms of  $[\text{Co}^{3+}(en)_2\text{Br}_2]^+$  ion are given at (a) and (b) of Fig. 7.14 respectively. Since the structure of cis-isomer and its mirror image are non-super imposable on each other, cis-isomer is unsymmetrical. On the other hand, since the structure of trans-form and its mirror image are superimposable on each other, trans-isomer is symmetrical. Thus cis-isomer is optically active but trans-isomer is optically inactive.

9. Octahedral complexes of [M(AA)2ab] type: [Co<sup>3+</sup>(en)<sub>2</sub>(NH<sub>3</sub>)Cl]<sup>2+</sup> is an important example of octahedral complex of [M(AA)<sub>2</sub>ab] type. This complex ion exists in cisand trans-isomers. In cis-isomer the two monodentate ligands viz., NH<sub>3</sub> and Cl<sup>-</sup> occupy the adjacent (i.e., cis) positions while in trans-isomer these ligands occupy opposite (i.e., *trans*) position (See Fig. 7.15).  $[Ru^{3+}(C_3O_4)_2(py)(NO_2)]^{2-}$ also exists in cis- and trans-isomers.





(a) Structure of cis-isomer of [Co(en),Br,]<sup>⊕</sup> and its mirror image

(b) Structure of trans-isomer of [Co(en)<sub>2</sub>Br<sub>2</sub>]<sup>⊕</sup> ion and its mirror image

Fig. 7.14 Structure of cis-and trans-forms of  $[Co(en)_2Br_2]^{\oplus}$  ion and their mirror images.

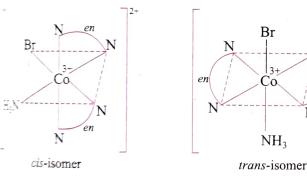


Fig. 7.15 cis-and trans-isomers of  $[Co^{3+}(en)_2(NH_3)(Br]^{2+}$  ion

As in case of  $[Co^{3+}(en)_2Cl_2]^{\oplus}$  ion, the *cis*-isomer of [Co<sup>3+</sup>(en)<sub>2</sub>(NH)<sub>3</sub>(Cl)]<sup>2+</sup> is also unsymmetrical while its trans-isomer is symmetrical. Thus cis-form is optically active while trans-isomer is optically inactive.

- 10. Octahedral complexes of  $[M(AA)a_2b_2]$  type: In this complex AA represents a bidentate ligand in which two A atoms are donor atoms, a and b are monodentate ligands. Octahedral complexes of  $[M(AA)a_2b_2]$  type exist in three geometrical isomers.
  - (i) One cis-isomer: In this isomer the two a groups are cis to each other. Similarly, the two b groups are also cis to each other. This isomer is unsymmetrical and has no mirror plane passing through the metal (M) or centre of inversion. Being unsymmetrical, this isomer is optically active.
  - (ii) Two trans-isomers: In one trans-isomer the two a groups are trans to each other and the two b groups are cis to each other. In the other trans-isomer the two

a groups are cis to each other and the two b groups are trans to each other. Both these isomers have mirror plane passing through the metal (M), AA and a, a/b, b and hence these give only super imposable mirror image. Both these isomers are symmetrical and hence are optically active, i.e., archiral.

**Examples:**  $[Co^{3+}(en)(NH_3)_2Cl_2]^+$  and  $[Co^{3+}(C_2O_4)]^+$ (NH<sub>3</sub>)<sub>2</sub>(NO<sub>2</sub>)<sub>2</sub>] are important examples of octahedral complex of  $[M(AA)a_2b_2]$ .

Geometrical isomers of [Co<sup>3+</sup>(en)(NH<sub>2</sub>)<sub>2</sub>Br<sub>2</sub>]<sup>+</sup> ion. This ion is an octahedral ion of [M(AA)a,b,] type. This ion has three geometrical isomers.

- (i) One cis-isomer. In this isomer two NH, ligands are cis to each other. Similarly, the two Br ligands are also cis to each other. [See Fig. 7.16]. This isomer is unsymmetrical and has no mirror plane passing through the metal or centre of inversion. Being unsymmetrical this isomer is optically active.
- (ii) Two trans-isomers. In one trans-isomer two NH<sub>3</sub> ligands are trans to each other and two Br ligands are cis to each other (See Fig. 7.16). In the other transisomer two NH<sub>3</sub> ligands are cis to each other and two  $\mathrm{Br}^{\odot}$  ligands are *trans* to each other (See Fig. 7.16). Both these isomers have mirror plane passing through the metal, en and NH<sub>3</sub>, NH<sub>3</sub>/Br<sup>©</sup>, Br<sup>©</sup> and hence these give only super-imposable mirror image. Both these isomers are symmetrical and are, therefore, optically active, i.e., archiral.

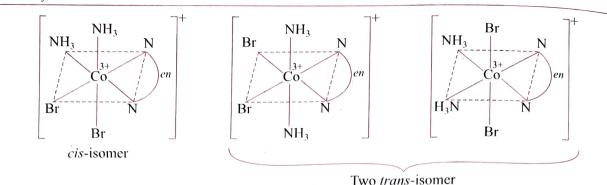


Fig. 7.16 cis-and trans-isomers of  $[Co^{3+}(en)(NH_2)_2Br_2]^{\oplus}$  ion

11. Octahedral complexes of [M(AB)<sub>3</sub>] type: Here (AB) represents an unsymmetrical bidentate ligand in which A and B are two different coordinating (donor) atoms. Octahedral complexes of this type exist in *cis-* and *trans-*isomers. As an example, the *cis-* and *trans-*isomers of [Cr<sup>3+</sup>(gly)<sub>3</sub>] have been shown in Fig. 7.17. Each of these forms is optically active and hence each has a pair of optical isomers. In *cis-*isomers two N-atoms and two O-atoms of two gly ions are placed at *cis-*positions while in *trans-*isomer these atoms are occupying *trans-*positions.

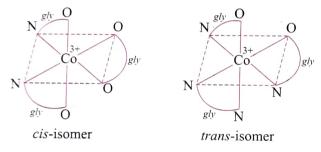


Fig. 7.17 cis- and trans-isomers of [Cr2+(gly)]

Since both the forms (i.e., *cis*- and *trans*-forms) are optically active, each of these forms had *d*-and *l*-forms (optical isomers).

## 7.8.2.5 Optical (or d-l or Mirror-Image) Isomerism

Before discussing the optical isomerism shown by various type of complexes we will define some important terms related to this isomerism.

- 1. Optical activity and optically active complexes: When the solutions of certain complex compounds are placed in the path of a plane-polarized light (the waves of the plane-polarized light vibrate only in one direction; vibrations in other directions are cut off), they rotate its plane through a certain angle which may be either to the left or to the right. This property of a complex of rotating the plane of polarized light is called its optical activity and the complex possessing this property is said to be optically active.
- 2. Different forms of optically active complexes: Optically active complexes are said to exist in the following forms:
  - (i) The isomer which rotates the plane of polarized light towards right (i.e., in clockwise direction) is said to be dextrorotatory or *d*-form, *d*-form is also represented by placing (+) sign before its name or formula.

- (ii) The isomer which rotates the plane of polarized light towards left (i.e., in anti-clockwise direction) is called levorotatory or *l*-form, *l*-form is also represented by putting (–) sign before its name or formula, (+), dextro, and (–), levo, refer to the sign of rotation of the optical isomer at the sodium D line wavelength. The *d* and *l*-forms have the following characteristics:
  - (a) Since *d*-and *l*-forms are capable of rotating the plane of polarized light, these are said to be optically active forms or optical isomers and this phenomenon is called optical activity or optical isomerism. These two forms have exactly identical physical and chemical properties, although they differ in their action on polarized light.
  - (b) *d*-and *l*-forms are mirror images to each other just as left hand is the mirror image of the right hand. Thus *d*-and *l*-forms can be superimposed on each other and hence *d*-and *l*-forms are also called mirror-image isomers. These optical isomers are also called optical antipodes or enantiomorphs (Latin; enantio = opposite; morphs = forms) or enantiomers. From this description it follows that optical isomerism can also be called mirror-image isomerism or enantiomorphism or enantiomerism.
- (iii) The isomer which is not capable of rotating the plane of polarized light is called optically inactive. Such an isomer is called meso, recemic, *dl*-or (±) form. A racemic substance is composed of 50% *d*-and 50% *l*-form. The solution of a racemic (*dl* mixture) form in a solvent which contains equimolecular amounts of *d* and *l*-forms is symmetrical and hence optically inactive, because the rotation (of the plane of polarized light) produced by one isomer, *d*-isomer, is balanced or compensated by equal but opposite rotation produced by the other (i.e., *l*-isomer). Optical inactivity produced in *dl*-mixture said to be due to external compensation.
- 3. Condition for a molecule to show optical isomerism: A molecule in which the grouping of the atoms is asymmetric is called an *asymmetric* or *dissymmetric molecule*. An asymmetric molecule has the following features:
  - (i) An asymmetric molecule never has a plane of symmetry (also called mirror-image plane) which is defined as an imaginary plane dividing the molecule in such a way that

the part of it on one side of the plane is the mirror image of that on the other side of the plane. The molecules possessing such a plane of symmetry are always inactive while those having no plane of symmetry are optically active and hence show optical isomerism.

(ii) An asymmetric molecule cannot be superimposed on its mirror image.

the most necessary and sufficient condition for a molecule policy optical isomerism (i.e., to exist in *d*-and *l*-forms) is that molecule should be asymmetric, (i.e., it should have no plane molecule and should be not be superimposable on its mirror of the most necessary and should be not be superimposable on its mirror of the most necessary and sufficient condition for a molecule policy of the most necessary and sufficient condition for a molecule policy of the most necessary and sufficient condition for a molecule policy of the most necessary and sufficient condition for a molecule policy of the most necessary and sufficient condition for a molecule policy of the most necessary and sufficient condition for a molecule policy of the most necessary and sufficient condition for a molecule policy of the most necessary and sufficient condition for a molecule policy of the most necessary and sufficient condition for a molecule policy of the most necessary and sufficient policy of the most necessary and the most nece

## Optical Isomerism in Tetrahedral Complex (C.N. = 4)

Here we shall discuss optical isomerism in the following of grahedral complexes.

- 1. Tetrahedral complexes of [Ma<sub>4</sub>], [Ma<sub>2</sub>b<sub>2</sub>] and [Ma<sub>3</sub>b] type: Tetrahedral complexes of [Ma<sub>4</sub>], [Ma<sub>2</sub>b<sub>2</sub>] and [Ma<sub>3</sub>b] type are not able to show optical isomerism because all the possible arrangements of the ligands round the central metal ion. M, are exactly equivalent.
- 2. **Tetrahedral complexes of [Mabcd] type:** Since the central atom (M) in tetrahedral complexes of [Mabcd] type is surrounded by four different ligands, the tetrahedral complex of this type is expected to produce a pair of enantiomorphs. For example,  $[As^{3+}(CH_3)(C_2H_6)(S)(C_6H_4COO)]^2$  ion (tetrahedral) exists in two optical isomers as shown in Fig. 7.18.

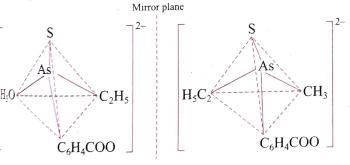


Fig. 7.18 Optical isomers of tetrahedral complex ion,  $[As(CH_3)(C_2H_5)(S)]$   $(C_6H_4COO)]^2$ 

Here it may be noted that 4 different groups the central metal ion are not the only requirement to make the complex to show mirror-image isomerism. All that is required is that the molecule should be asymmetric (i.e., unsymmetrical), i.e., it should have no plane of symmetry so that it can exist in two mirror-image forms.

3. Tetrahedral complexes of Be (II), B (III) and Zn (II) with symmetrical bi-dentate ligands have been made and resolved into optical isomers. Some examples of tetrahedral complexes of this type are *bis* (salicylaldehydato) boron (III) ion, [B<sup>3+</sup>(C<sub>6</sub>H<sub>4</sub>.O.CHO)<sub>2</sub>]<sup>+</sup> and *bis* (benzoylacetonato) beryllium (II), [Be<sup>2+</sup>(C<sub>6</sub>H<sub>5</sub>CO.CH.CH<sub>3</sub>CO)<sub>2</sub>]<sup>0</sup> whose mirror-image isomer are given in Fig. 7.19 and 7.20 respectively.

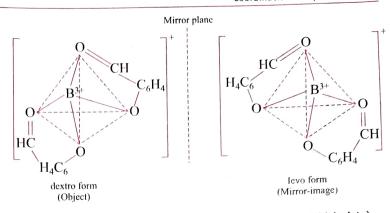


Fig. 7.19 Mirror-image isomers of tetrahedral bis (salicylaldehydato) boron (III) ion, [B³+(C₄H₆.O.CHO)₂]<sup>+</sup>

Mirror plane

 $\begin{array}{c|cccc} CH_3 & CH_3 & CH_3 & CH_3 \\ C& & C& C\\ C& & Be & C-H & H-C & Be & C-H\\ C& & & C& C\\ C_6H_5 & & & C& C_6H_6 & C& C_6H_6 \\ & & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & \\ & &$ 

Fig. 7.20 Mirror-image isomers of tetrahedral bis (benzoylacetonato) beryllium (II) ion,  $\left[Be^{2+}(C_6H_5C0.CHCH_3C0)_2\right]^0$ 

## 7.8.2.7 Optical Isomerism in Square Planar Complexes (C.N. = 4)

Optical isomerism rarely occurs in square planar complexes, since they have all the four ligands and the central metal ion in the same plane and hence contain a plane or axis of symmetry. Thus these complexes are optically inactive, i.e., they cannot show optical isomerism even if all the four ligands are different.

### 7.8.2.8 Optical Isomerism in Six-Coordinated Complexes

Octahedral complexes: Here we shall discuss the optical in octahedral complexes of the following type:

- 1. Octahedral complexes of [Ma<sub>6</sub>] and [Ma<sub>5</sub>b] type: Complexes of this type do not show optical isomerism.
- 2. Octahedral complexes of [Ma<sub>4</sub>b<sub>2</sub>] and [Ma<sub>3</sub>b<sub>3</sub>] type: (a) We have already seen that octahedral complexes of [Ma<sub>4</sub>b<sub>2</sub>] type exist in *cis* and *trans*-isomers. Both these isomers are optically inactive due to the presence of symmetry and hence do not show optical isomerism, (b) We have already mentioned that octahedral complexes of [Ma<sub>3</sub>b<sub>3</sub>] type exist in cis (or facial) and trans (or meridional) isomers. Both these isomers are optically inactive and hence do not show optical isomerism.
- 3. Octahedral complexes of [Ma<sub>2</sub>b<sub>2</sub>c<sub>3</sub>] type: Complexes of this type do not show optical isomerism.
- 4. Octahedral complexes of [Ma<sub>2</sub>b<sub>2</sub>c<sub>2</sub>] type: [Pt<sup>4+</sup>(NH<sub>3</sub>)<sub>2</sub>(py)<sub>2</sub>Br<sub>2</sub>]<sup>2+</sup> ion is an important example of octahedral complex of [Ma<sub>2</sub>b<sub>2</sub>c<sub>2</sub>] type. We have already stated that [Pt<sup>4+</sup>(NH<sub>3</sub>)<sub>2</sub>(py)<sub>2</sub>Br<sub>2</sub>]<sup>2+</sup> ion can exist theoretically in five geometrical isomers, but only three have been

isolated. In *cis*-isomer two identical ligands occupy the adjacent positions of the octahedron. This *cis*-isomer exists in two optical (mirror-image) isomers which are mirror-image to each other as shown in Fig. 7.21. *Trans*-form of this complex ion is symmetrical and hence is optically inactive form. Thus it is *trans-meso* form.

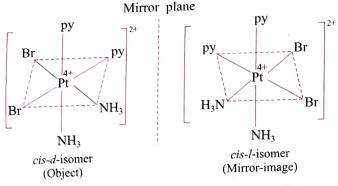


Fig. 7.21 Mirror-image isomers of  $[Pt^{4+}(NH_3)_2(py)_2Br_2]^{2+}$  ion

5. [Mabcdef] type complexes:  $[Pt^{4+}(py)(NH_3)(NO_2)ClBr_2]^0$  is the only example of octahedral complex of this type. We have already stated that, theoretically, this complex can exist in 15 geometrical isomers. Each of these 15 geometrical isomers exists in optically active *d*-and *l*-forms, giving a total of 30 optically active isomers, *d*-and *l*-isomers for one of the 15 geometrical isomers are given in Fig. 7.22.

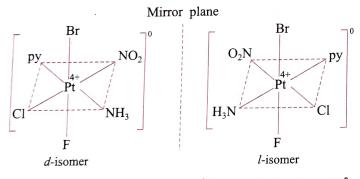


Fig. 7.22 Optical (d-and l-) forms of  $[Pt^{4+}(py)(NH_3)(NO_2)(Cl)(Br)(I)]^0$ 

6. [M(AA)<sub>3</sub>] type complexes: Due to the absence of a plane

or centre of symmetry, the octahedral complexes of this type are resolvable into dextro and levo forms. For example, d-and l-forms of  $[Co^{3+}(en)_3]^{3+}$  ion are shown in Fig. 7.23. Other examples of octahedral complexes of  $[M(AB)_3]$  type which exist in d and l forms are:  $[Cr^{3+}(ox)_3]^{3-}$ ,  $[Co^{3+}(pn)_3]^{3+}$ ,  $[Pt^{4+}(en)_3]^{4+}$ ,  $[Fe^{2+}(diph)_3]^{2+}$  etc. The fact that the complexes of  $[M(AA)_3]$  type can be resolved into optical isomers confirms that these complexes have octahedral shape. Neither hexagonal nor trigonal prismatic geometry of 6-coordinated complex can give rise to activity.

7. [M(AA)<sub>2</sub>a<sub>2</sub>] type complexes: Here we can consider [Co<sup>3+</sup>(en)<sub>2</sub>Cl<sub>2</sub>]<sup>+</sup> ion. We have already stated that this ion shows geometrical isomerism and hence exists as cis- and trans-isomers. The cis-isomer does not have any plane or centre of symmetry and hence is optically active, i.e., cis-isomer can be resolved into two optically active isomers (d- and l-isomers). On the other hand, the trans-isomer has a plane of symmetry and hence is optically inactive, i.e., it cannot be resolved into optically active isomers.

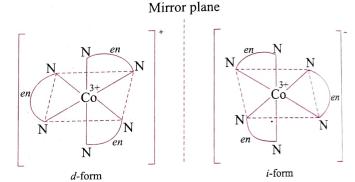


Fig. 7.23 Optical isomers of  $[{\rm Co}^{3+}({\rm en})_5]^{2-}$  ion. These cannot be superimposed on each other

Thus trans-isomer is optically inactive (meso-form). Consequently  $[Co(en)_2Br_2]^+$  ion has three optical isomers viz. (a) Two optically active isomers corresponding to cis-configuration (i.e., d-and l-forms). One form is the mirror image of the other. (b) One optically inactive form corresponding to trans-form (meso-form). All the three forms have been shown in Fig. 7.24.

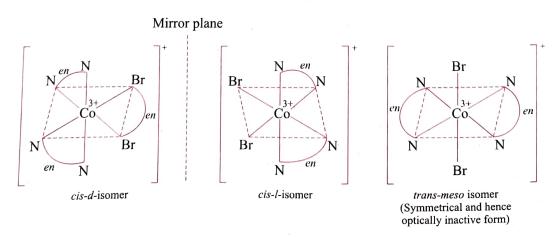


Fig. 7.24 Optical isomers of  $[Co(en)_2Br_2]^{\oplus}$  ion

Other examples of [M(AA)<sub>2</sub>a<sub>2</sub>] type octahedral complexes whose cis-isomers exist in dextro (d) and levo (l) forms are: whose cas fishers since in decade (a) and leve (1) forms are:  $[C_0^{3+}(en)_2(NO_2)_2]^+, [Ir^{4+}(C_2O_4)_2Cl_2]^{2-}, [Rh^{4+}(C_2O_4)_2Cl_2]^{2-}, [C_1^{3+}(C_2O_4)_2(H_2O)_2]^{-1}, [Ir^{3+}(C_2O_4)_2Cl_2]^{3-} etc.$ 

 $M(AA)_2$ ab] type complexes: Here we shall consider  $M(AA)_2$ ab] type complexes:  $M(AA)_$ 

exists in cis- and trans-isomers (geometrical isomers). Due to the absence of plane or centre of symmetry in cis-isomer, this isomer is optically active and hence can be resolved into d- and l-forms. On the other hand, the trans-isomer has a plane of symmetry and hence is optically inactive, i.e., trans-isomer is meso-trans isomer (See Fig. 7.25).

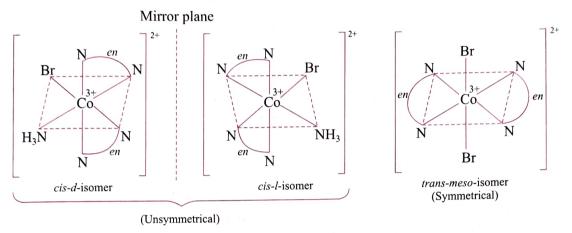


Fig. 7.25 Optical isomers of  $[{\rm Co}^{2+}({\rm en})_2({\rm NH}_3){\rm Br}]^{2+}$  ion

Another example of  $[M(AA)_2ab]$  type octahedral complexes whose cis-isomer exists in d- and l-forms is  $[Rh^{3+}(C_2O_4)_2(py)(NO_2)]^{2-}$ . 9.  $[M(AA)a_2b_2]$  type complexes: Here we shall consider  $[Co^{3+}(en)(NH_3)_2Br_2]^{\oplus}$  ion. We have seen that this ion exists in *cis-* and trans-isomers (geometrical isomers). Cis-isomer is optically active and hence gives optically active d- and l-forms. On the other hand trans-isomer is optically inactive and hence does not give any optical active isomer, (See Fig. 7.26).

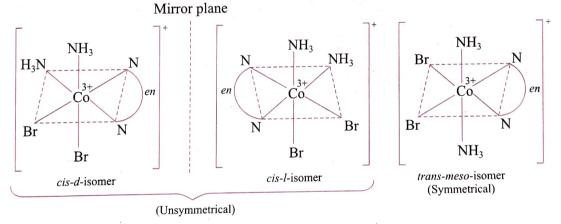


Fig. 7.26 Optical isomers of  $[Co^{3+}(en)(NH_3)_2Br_2]^{\oplus}$  ion

 $[\text{Co}^{3+}(\text{C}_2\text{O}_4)(\text{NH}_3)_2(\text{NO}_2)_2]^-$  ion is another important example of  $[\text{M}(\text{AA})a_2b_2]$  type octahedral complexes whose *cis*-isomer gives *d*- and *l*-isomers.

10. [M(AB)<sub>3</sub>] type complexes: We have seen that an octahedral complex of this type exists in cis- and trans-isomers (geometrical isomers). Each of these forms is optically active and hence each gives a pair of optical isomers (d- and l-forms) as shown in Fig. 7.27 for [Cr<sup>3+</sup>(gly)<sub>3</sub>] complex compound.

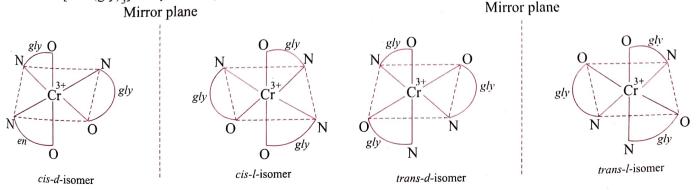


Fig. 7.27 Each of cis-and trans-isomers of  $[Cr^{3+}(gly)_{\circ}]^{0}$  has d and l optical isomers

Table 7.14 Summary of Geometrical and optical isomerism shown by octahedral complexes (C.N. = 6)

The state of the s	f octahedral mplex	Examples	Geometrical isomerism	Optical isomerism
1. [N	Ma <sub>6</sub> ]	Special Services	. X	×
	Ma <sub>s</sub> b]		×	×
	Ma <sub>4</sub> b <sub>2</sub> ]	$[Cr^{3+}(NH_3)Cl_2]^+,$ $[Co^{3+}(NH_3)_4Cl_2]^+$ etc.	cis- and trans-isomers	X
4. [N	/a <sub>3</sub> b <sub>3</sub> ]	$[\text{Co}^{3+}(\text{NH}_3)_3\text{Cl}_3]^0$ , $[\text{Rh}^{3+}(py)_3\text{Cl}_3]^0$ etc.	cis-(or fac) and trans-(or mer) isomers	X
5. [N	Λa₄bc]	$[\text{Co}^{3+}(\text{NH}_3)_2(\text{H}_2\text{O})(\text{Cl})]^{2+}$	cis- and trans-isomers	X
	$Ma_2b_2c_2$	$[Pt^{4+}(NH_3)_2(py)_2Cl_2]^{2+}$	Five geometrical forms. Only three have been isolated	meso form
7. [N	Mabcedef]	[Pt <sup>3+</sup> (NH <sub>3</sub> )(Cl)(Br)(I) (NO <sub>2</sub> )(py)] <sup>0</sup>	15 different geometrical isomers	Each geometrical isomer has <i>d</i> - and <i>l</i> -isomers. Thus we have 30 optical isomers
8. [N	$M(AA)_3$	$[\text{Co}^{3+}(en)_3]^{3+}$ etc.	×	d- and l-isomers
Control of the least	$M(AA)_2 a_2$	$[\operatorname{Co}^{3+}(en)_3\operatorname{Cl}_2]^+ \text{ etc.}$	cis- and trans-isomers (cis- isomers is unsymmetrical)	Being unsymmetrical, <i>cis</i> -isomer gives <i>cis-d-</i> and <i>cis-l-</i> isomers (optical isomers)
10. [N	M(AA) <sub>2</sub> ab]	$[\text{Co}^{3+}(en)_2(\text{NH}_3)(\text{Cl})]^{2+}$ etc.	cis- and trans-isomers	Being unsymmetrical, <i>cis</i> -isomer gives <i>cis-d</i> and <i>cis-l</i> -isomers (optical isomers)
11. [M	1(AA)a <sub>2</sub> b <sub>2</sub> ]	$\left[\mathrm{Co}^{3+}(en)(\mathrm{NH}_3)_2\mathrm{Cl}_2\right]^+ \mathrm{etc.}$	cis- and trans-isomers	cis-isomer exists as cis-d-and cis-l-isomer (optical isomers)
12. [M	M(AB) <sub>3</sub> ]	$\left[\operatorname{Cr}^{3+}(\operatorname{gly})_{3}\right]^{0}$	cis- and trans-isomers (Each form is optically active)	Each geometrical form is optically active. Hence cis-form gives cis-d-and cis-l-optical isomers. Similarly trans-form gives trans d- and trans-loptical isomers.

Table 7.15 Summary of geometrical and optical isomerism shown by tetrahedral and square planar complexes (C.N. = 4)

Types of complexes	Geometrical isomerism	Optical isomerism
(A) Tetrahedral complexes		
1. [Ma <sub>4</sub> ]	×	×
2. [Ma <sub>3</sub> b]	×	×
3. [Mabcd] e.g.[ $As^{3+}(CH_3)(C_2H_5)(S)(C_6H_4COO)$ ] <sup>2-</sup>	×	Two optical isomer
4. Complexes of Be(II), B(III) etc. containing unsymmetrical bi-dentate ligands e.g. [Br <sup>2+</sup> (C <sub>6</sub> H <sub>5</sub> CO.CH.CH <sub>3</sub> CO) <sub>2</sub> ] <sup>0</sup> and [B <sup>3+</sup> (C <sub>6</sub> H <sub>4</sub> OCHO) <sub>2</sub> ] <sup>+</sup>	×	d- and l-isomer
B) Square planar complexes  1. [Ma <sub>4</sub> ]	×	Square planar complexes rarely show
2. [Ma <sub>3</sub> b]	X	optical isomerism
3. [Mab <sub>3</sub> ]	×	
4. $[Ma_2b_2]$ e.g. $[Pt^{2+}(NH_3)_2Cl_2]^0$	cis- and trans-isomers	
5. [Mabcd] e.g. $[Pt^{2+}(NH_3)(py)(Cl)(Br)]^0$	Three isomeric forms	
6. $[Ma_2bc]$ e.g. $[Pd^{2+}Cl_2BrI]^{2-}$ , $[Pt^{2+}(py)_2(NH_3)(Cl)]^+$	cis- and trans-isomers	
7. $M(AB)_2$ e.g. $[Pt^{2+}(gly)_2]^0 (gly^- ion is NH_2CH_2COO^-)$	cis- and trans-isomers	

#### Note:

- 1. Characteristics of square planar complexes
  - (i) These have plane of symmetry. (ii) These are optically inactive.
- 2. Characteristics of tetrahedral complexes.
  - (i) These do not have any plane of symmetry i.e., these are asymmetric. (ii) These are optically active.
- 3. *cis*-isomers (geometrical isomer) is asymmetrical and hence is optically active. Being optically active, *cis*-isomer has *d-cis* and *l-cis* isomers (optical isomers).
- 3. trans-isomer (geometrical isomer) is symmetrical and hence is optically inactive. Being optically inactive, trans-isomer is transmeso form.

## ILLUSTRATION 7.18

why is geometrical isomerism not possible in tetrahedral complexes having two different types of unidentate ligands coordinated with central metal ion?

Tetrahedral complexes do not show geometrical isomerism the relative positions of the unidentate ligands attached central metal atom are the same with respect to each other.

## ILLUSTRATION 7.19

In the reaction,  $[CoCl_2(NH_3)_4]^{\oplus} + Cl^{\ominus} \longrightarrow [CoCl_3(NH_3)_3] + NH_3$ , only one isomer of the complex product is obtained. Is the initial complex ris or trans?

In the original complex, two  $Cl^{\Theta}$  ions are present in the position, so that all four NH<sub>3</sub> molecules are equivalent and polacement of any one of them gives same product.

$$\begin{bmatrix} H_{3}N & Cl & NH_{3} \\ H_{3}N & Cl & NH_{3} \end{bmatrix}^{\oplus} + Cl^{\ominus} - \begin{bmatrix} Cl & NH_{3} \\ H_{3}N & Cl & NH_{3} \end{bmatrix}^{\oplus} + NH_{3}N + NH_{3}$$

#### LLUSTRATION 7.20

When  $[\mathrm{Ni}(\mathrm{NH_3})_4]^{2^+}$  is treated with conc. HCl, two compounds having the formula  $\mathrm{Ni}(\mathrm{NH_3})\mathrm{Cl_2}$  (designated as I and II are formed). I can be converted into II by boiling in dil. HCl. A solution of I reacts with oxalic acid to form  $\mathrm{Ni}(\mathrm{NH_3})_2(\mathrm{C_2O_4})$ . I does not react with oxalic acid. Deduce the configuration of land II and the geometry of Ni(II) complexes.

$$[Ni(NH_3)_4]^{2+} + HCl \longrightarrow Ni(NH_3)_2Cl_2$$

conc. (I and II)

 $I \xrightarrow{\text{dil. HCl}} II$ 

 $I \xrightarrow{\text{Oxalic acid}} \text{Ni(NH}_3)_2(\text{C}_2\text{O}_4)$ 

∏ Oxalic acid No reaction

 $^{C_2O_4^{2-}}$  ion is acting as a bidentate ligand, and forms chelate ring, since I isomer of Ni(NH<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> form Ni(NH<sub>3</sub>)<sub>2</sub>C<sub>2</sub>O<sub>4</sub> this indicates two Cl<sup> $\Theta$ </sup> ions in I are present at cis-position.

$$\begin{array}{c|c} H_{3}N & O & O & O \\ \hline & H_{3}N & O & C \\ \hline & H_{3}N & O & C \\ \hline & H_{3}N & O & C \\ \hline & O & H_{3}N & O & C \\ \hline & O & O & O \\ \hline & O &$$

II isomer of Ni(NH<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> does not react with  $C_2O_4^{2-}$  ion means that the 2 Cl<sup> $\Theta$ </sup> are present at trans position.

Hence I is

cis-diamminedichloridonickel(II)

and II is

trans-diamminedichloridonickel(II)

#### ILLUSTRATION 7.21

How can the following pair of isomers be distinguished from one another?

- **a.** I.  $[Co(NH_3)_6][Cr(NO_2)_6]$  and
  - II.  $[Cr(NH_3)_6][Co(NO_2)_6]$
- **b.** I.  $[Cr(NH_3)_6][Cr(NO_2)_6]$  and
  - II.  $[Cr(NH_3)_4(NO_2)_2][Cr(NH_3)_2(NO_2)_4]$

#### Sol.

**a.** I can be distinguished from II by electrolysis of their aqueous solution.

(I) 
$$\xrightarrow{\text{Electrolysis}} [\text{Co(NH}_3)_6]_{(\text{aq})}^{3+} + [\text{Cr(NO}_2)_6]_{(\text{aq})}^{3-}$$

 $[Co(NH_3)_6]^{3+}$  will migrate towards anode and is deposited on anode.

(II) 
$$\longrightarrow$$
  $[Cr(NH_3)_6]_{(aq)}^{3+} + [Co(NO_2)_6]_{(aq)}^{3-}$ 

On electrolysis,  $[Cr(NH_3)_6]^{3+}$  ion will move towards anode and is deposited on anode.

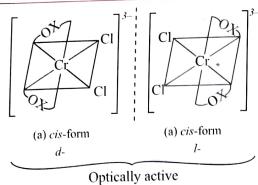
**b.** (I) and (II) can be distinguished by conducting measurements (I) will show conductivity as (3+, 3-) electrolyte whereas (II) will conduct electricity as (+1, -1) electrolyte.

#### ILLUSTRATION 7.22

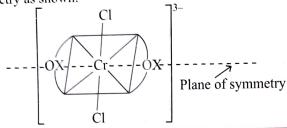
Out of the following two coordination entities which is chiral (optically active)?

- a.  $\operatorname{cis-[CrCl_2(OX)_2]^{3-}}$
- **b.** trans- $[CrCl_2(OX)_2]^{3-}$

**Sol.** The two geometrical isomers (a) and (b) are of the type  $[M(AA)_2 b_2]^{n\pm}$ , so (a) **cis-isomer** is chiral (optically active). The two entities are represented as:

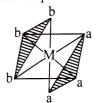


**Trans-form** is optically inactive, due to the presence of plane of symmetry as shown:



11.  $[Ma_3b_3]^{n\pm}$ . e.g.  $[CoCl_3(NH_3)_3]$ 

Such complexes do not show optical isomerism.





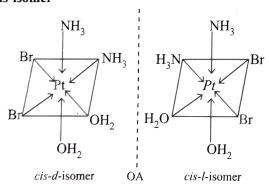
cis- or facial (fac)

trans or Meridoinal (mer)

OIA (Optically inactive isomers)

**12.**  $[Ma_2b_2c_2]^{n\pm}$ , e.g.  $[Pt(NH_3) (H_2O)_2 Br_2]^{2+}$ 

cis-isomer



Optically active due to non-superimposable mirror image.

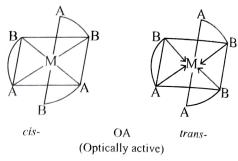
13. [Mabcdef]<sup> $n\pm$ </sup>: If the central atom is asymmetrically coordinated, each of its 15 geometrical isomers should be resolved into optical isomers, e.g.

 $[PtClBr\ (NH_3)\ (NO_2)\ (py)I]$ 

Only 3 isomers have been prepared till now, no form has been resolved.

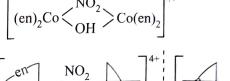
- 14.  $[Mabcd(AA)_2]^{n\pm}$  type e.g.,  $[Cr^{+3}Br^{-1}Cl^{-1}(CN^{-1})(H_2O^0)(en^0)]$ shows 12 optically active isomers.
- **15.**  $[Ma_2b_2(gly)]^{n\pm}$  type e.g.,  $[Cr^{+3}Cl_2^{-2}Br_2^{-2}(gly^{-1})]^{2-}$  shows 4 optically active isomers.

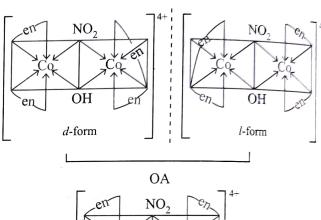
16.  $[M(AB)_3]^{n\pm}$ : AB is unsymmetrical bidentate ligand, e.g.

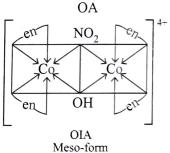


Both forms are optically active.

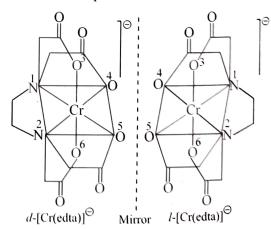
17. Polynuclear complexes also show optical activity, e.g.







**18.** Octahedral complexes containing hexadentate ligands, e.g., [Cr(edta)]<sup>⊖</sup>, i.e., ethylene diaminetetraacetato chromate(III) ion, also shows optical isomerism.



**Note:** The total number of N-Cr-O bond angles in  $[Cr(edta)]^{\Theta}$  complex ion is 8, as shown below.

There are 2N-atom ( $N^1$  and  $N^2$ ) and 4 O-atom ( $O^3$ ,  $O^4$ ,  $O^5$ ,  $O^6$ ). So total 8 N–Cr–O bond angle are possible as given below:

- $1. N^1$ –Cr– $O^3$
- 2. N<sup>1</sup>-Cr-O<sup>4</sup> 3. N<sup>1</sup>-Cr-O<sup>5</sup> 4. N<sup>1</sup>-Cr-O<sup>6</sup>
- 5.  $N^2$ –Cr– $O^3$
- 6.  $N^2$ -Cr- $O^4$  7.  $N^2$ -Cr- $O^5$  8.  $N^2$ -Cr- $O^6$

## Moreover, (N-Cr-N) bond angle = 1

(O-Cr-O) bond angle = 6.

## LUSTRATION 7.23

Write the structure and name of the following and their coordination isomers.

- (A) [Co(en)<sub>3</sub>] [Cr(CN)<sub>6</sub>]
- (B) [Co(NH<sub>3</sub>)<sub>6</sub>] [Cr(C<sub>2</sub>O<sub>4</sub>)<sub>3</sub>]
- i. The coordination isomer of (A) is [Cr(en)<sub>3</sub>] [Co(CN)<sub>6</sub>]. The structure and name of the above two isomers are given below:
  - (A) ⇒ Tris (ethylenediamine)cobalt(III)

hexacyanochromate (III) and its isomer

Tris (ethylenediamine) chromium(III) hexacyanocobaltate

- ii. Coordination isomer of (B) is  $[Cr(NH_3)_6][Co(C_2O_4)_3]$ . The structure and name of these isomers are given below:
  - (B) ⇒ Hexamminecobalt(III) tris (oxalato)chromate(III) and its isomer.

 $[Cr(NH_3)_6][Co(C_2O_4)_3]$  is

Hexamminechromium(III) tris (oxalato)cobaltate(III).

#### LUSTRATION 7.24

Draw the structures and write the names of all possible linkage

- i. (A)  $[Pt(SCN) (NH_3)_3] SCN$
- ii. (B)  $[Co(SCN) (NH_3)_5] Cl_2$
- iii. (C)  $[Co(NH_3)_5(NO_5)]^{2+}$

i. (A) has one linkage isomer  $A_1$  which is

 $[Pt(NCS)(NH_3)_3]SCN$ . In  $(A_1)$ ,  $\Theta$ SCN ion (ligand) is linked with Pt2+ ion (central metal ion) through negatively-charged N-atom. Thus the structures and names of these linkage isomers can be written as given below:

$$(A) \Rightarrow \begin{bmatrix} H_{3}N_{2} & NH_{3} \\ Pt^{2+} & NH_{3} \\ H_{3}N^{2} & SCN^{\Theta} \end{bmatrix}$$

$$SCN^{\Theta}$$

(Triamminethiocyanatoplatinum(II)thiocyanate)

$$(A^{1}) \Rightarrow \begin{bmatrix} H_{3}N_{7} - \cdots & NH_{3} \\ P_{1}^{2+} & \vdots \\ H_{3}N^{2} - \cdots & N\Theta = C = \ddot{S} \end{bmatrix}^{\oplus} SCN^{\Theta}$$

(Triammineisothiocyanatoplatinum (II) thiocyanate,

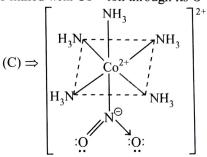
[(Pt (NCS) (NH<sub>3</sub>)<sub>3</sub>] SCN

ii.  $[Co(NCS)(NH_3)_5]Cl_2$ 

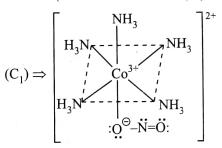
(Pentaammineisothiocyanato cobalt (III) chloride)

is the linkage isomer of [Co(SCN)(NH<sub>3</sub>)<sub>5</sub>]Cl<sub>2</sub> Pentaamminethiocyanato cobalt (Ill) chloride

iii. Since NO<sub>2</sub> ion is an ambidentate ligand, the given complex ion has two linkage isomers. The structures of these isomers are shown in figure. In (C)  $NO_2^{\Theta}$  ion (ligand) is linked with the central Co3+ ion through its N-atom while in its isomer (C<sub>1</sub>) it is linked with Co<sup>3+</sup> ion through its O-atom.



(Pentammininenitrocobalt (III) ion)



(Pentamminenitritocobalt (Ill) ion)

#### ILLUSTRATION 7.25

The complex ion [Co(NH<sub>3</sub>)<sub>5</sub>Cl]<sup>2+</sup>(X)undergoes a substitution reaction when reacted with (NaNO2 + HCl). An unstable scarlet red complex A is formed when dilute acid is used and a stable yellow complex B is formed when concentrated acid is used. Both A and B are isomeric pentammine complex ions. Give the structures of the ions und name the type of isomerism involved.

Sol. Since the treatment of (X) (NaNO<sub>2</sub> + dil. HCl) gives an unstable red complex, this red complex should be pentaammine nitritocobalt (III)ion, [Co<sup>3+</sup>(NH<sub>3</sub>)<sub>5</sub> (ONO)]<sup>2+</sup>.

Similarly, the ion obtained by treating  $[Co^{3+}(NH_3)_5 Cl]^{2+}(X)$ ion with (NaNO<sub>2</sub> + conc. HCl) should be pentaammine nitrocobalt (III) ion,  $[Co^{3+}(NH_3)_5(NO_2)]^{2+}$ 

Thus  $A = [Co^{3+} (NH_3)_5 (ONO)]^{2+}$  and

 $B = [Co^{3+} (NH_3)_5 (NO_2)]^{2+}.$ 

Obviously A and B linkage isomers and the isomerism involved is linkage isomerism.

### ILLUSTRATION 7.26

What type of isomers are the following:

- I. a.  $[Mn(CO)_5(SCN)]$  and  $[Mn(CO)_5(NCS)]$ 
  - b.  $[Co(en)_3][Cr(CN)_6]$  and  $[Cr(en)_3][Co(CN)_6]$
  - c.  $[Co(NH_3)_5NO_3]SO_4$  and  $[Co(NH_3)_5SO_4]NO_3$
  - d.  $[Co(py)_2(H_2O)_2Cl_2]Cl$  and  $[Co(py)_2(H_2O)Cl_3]\cdot H_2O$
- II. a.  $[Cr(NH_3)_6][Cr(CN)_6]$  and  $[Cr(NH_3)_4(CN)_2][Cr(NH_3)_2(CN)_4]$ 
  - b.  $[Pt(NH_3)_4Br_2]Cl_2$  and  $[Pt(NH_3)_4Cl_2]Br_2$

- a. The given complexes are linkage isomers, since these complexes have ambidentate ligand viz. SCN<sup>⊖</sup> ion.
  - b. The given complex compounds are **coordination isomers**, since each of them contains complex cation and complex anion as shown below and these complex compounds can be obtained by interchanging the ligands present in complex cation and complex anion.

Complex cation

Complex compound

[Co(en)<sub>3</sub>] [Cr(CN)<sub>6</sub>] 
$$\rightleftharpoons$$
 [Co(en)<sub>3</sub>]<sup>3+</sup> + [Cr(CN)<sub>6</sub>]<sup>3-</sup>

[Cr(en)<sub>3</sub>] [Co(CN)<sub>6</sub>]  $\rightleftharpoons$  [Cr(en)<sub>3</sub>]<sup>3+</sup> + [Co(CN)<sub>6</sub>]<sup>3-</sup>

c. These are **ionisation isomers**, since they give different ions in aqueous solution as shown below:

queous solution as shown below:
$$[\text{Co(NH}_3)_5\text{NO}_3]\text{SO}_4 \Longrightarrow [\text{Co(NH}_3)_5\text{NO}_3]^{2^+} + \text{SO}_4^{2^-}$$

$$(I)$$

$$[\text{Co(NH}_3)_5\text{SO}_4]\text{NO}_3 \Longleftrightarrow [\text{Co(NH}_3)_5\text{SO}_4]^{\oplus} + \text{NO}_3^{\ominus}$$

$$(II)$$

- (I) gives  $SO_4^{\ 2^-}$  ions and (II) gives  $NO_3^{\ \Theta}$  ions. Complex cations given by them are also different. Due to the production of  $SO_4^{\ 2^-}$  ions, (I) gives a white precipitate of  $BaSO_4$  with  $BaCl_2$  solution. On the other hand, (II) gives the test of  $NO_3^{\ \Theta}$  ions.
- d. These compounds are hydrate isomers, since they contain different number of H<sub>2</sub>O molecules inside and outside coordination sphere.

$$[\operatorname{Co(py)}_2(\operatorname{H}_2\operatorname{O})_2\operatorname{Cl}_2]\operatorname{Cl} \Longrightarrow [\operatorname{Co(py)}_2(\operatorname{H}_2\operatorname{O})_2\operatorname{Cl}_2]^{\oplus} + \operatorname{Cl}^{\ominus}$$
Electrolyte (I)

$$[Co(py)_2(H_2O)Cl_3] \cdot H_2O \rightleftharpoons$$
 No ionisation  
Non-electrolyte (II)

II. a. The given complex compounds are coordination isomers, since each of them contains complex cation and complex anion as shown below and these isomers can be obtained by interchanging their ligands.

$$\begin{array}{ccc} & Complex & Complex & Complex \\ compound & cation & anion \\ [Cr(NH_3)_6] [Cr(CN)_6] & \longleftarrow [Cr(NH_3)]^{3^+} + [Cr(CN)_6]^{3^-} \\ [Cr(NH_3)_4(CN)_2] [Cr(NH_3)_2(CN)_4] & \longleftarrow \\ & [Cr(NH_3)_4(CN)_2]^{\oplus} + [Cr(NH_3)_2(CN)_4]^{\ominus} \\ \end{array}$$

b. The given complex compounds are **ionisation isomers**, since they give different ions in aqueous solution as shown below:

(I) gives  $\mathrm{Cl}^{\Theta}$  ions and (II) gives  $\mathrm{Br}^{\Theta}$ ions. (I) gives white precipitate of  $\mathrm{AgCl}$  with  $\mathrm{AgNO_3}$  solution. On the other hand, (II) gives yellow precipitate of  $\mathrm{AgBr}$  with  $\mathrm{AgNO_3}$  solution.

## ILLUSTRATION 7.27

Draw all possible isomers of:

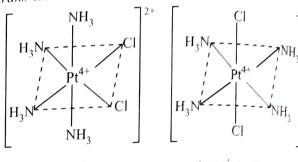
i.  $[Pt(NH_3)_4Cl_2]^{2+}$ 

iii. [Pt{P(C<sub>2</sub>H<sub>5</sub>)<sub>3</sub>}Cl<sub>2</sub>],

**ii.** [Pt(gly)<sub>2</sub>]<sup>0</sup> **iv.** [Cr(NH<sub>3</sub>) (OH)<sub>2</sub>Cl<sub>3</sub>]<sup>2</sup>-

#### Sol.

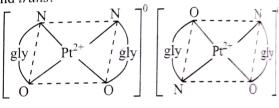
i.  $Pt(NH_3)_4Cl_2l^{2+}$  ion: This ion is an octahedral ion of  $[Ma_4b_2]$  type and hence has two geometrical isomers viz cis and trans isomers. In cis-isomer two  $Cl^{\Theta}$  ions are in cis-position and in trans-isomer these ions have trans position.



cis-isomer

trans-isomer

ii. [Pt(gly)<sub>2</sub>]<sup>0</sup>: It is a square planar complex of [M(AB)<sub>2</sub>] type in which gly<sup>⊙</sup> ion (NH<sub>2</sub>.CH<sub>2</sub>.COO<sup>⊙</sup>) is an unsymmetrical bidentate ligand. This complex has two geometrical isomers viz *cis* and *trans*.



cis-isomer

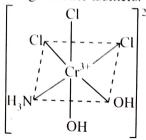
trans-isomer

iii. [Pt{P(C<sub>2</sub>H<sub>5</sub>)<sub>3</sub>}Cl<sub>2</sub>]<sub>2</sub>: It is a bridged binuclear planar complex and exists in three isomeric forms viz cis. trans and unsymmetrical.

Cl Pt Cl Pt 
$$P(C_2H_5)_3$$
 P  $P(C_2H_5)_3$  Cl Pt  $P(C_2H_5)_3$  Cl Pt  $P(C_2H_5)_3$  Promise  $P(C_2H_5)_3$  Promise  $P(C_2H_5)_3$  Cl Pt  $P(C_2H_5)_3$  Promise  $P(C_2H_5)_3$  Promise  $P(C_2H_5)_3$  Promise  $P(C_2H_5)_3$  Promise  $P(C_2H_5)_3$  Promise  $P(C_2H_5)_3$ 

unsymmetrical-isomer

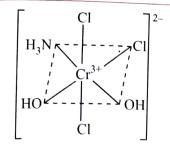
iv. [Cr(NH<sub>3</sub>) (OH)<sub>2</sub>Cl<sub>3</sub>]<sup>2-</sup> ion: [Ma<sub>3</sub>b<sub>2</sub>c]<sup>n±</sup> type. This ion has three geometric isomers.



a. Cl-Cl cis, OH-OH cis

$$\begin{bmatrix} Cl \\ OH_{2} - - - Cl \\ Cr^{3+} \\ - - OH \end{bmatrix}^{2}$$

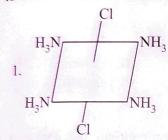
**b.** Cl–Cl trans, OH–OH trans

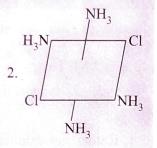


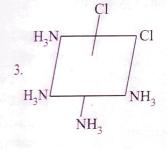
c. Cl-Cl trans, OH-OH cis

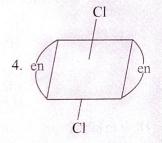
## ILLUSTRATION 7.28

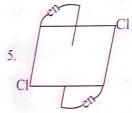
- I. Neither optical nor geometrical isomers can be distinguished by mass spectroscopy. Why?
- Il. Select the pairs of
  - a. Geometrical isomers
- b. Optical isomers
- c. Identical structures.

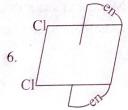


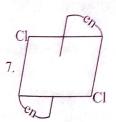


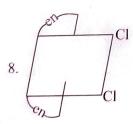






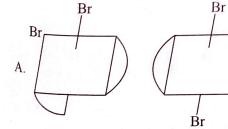


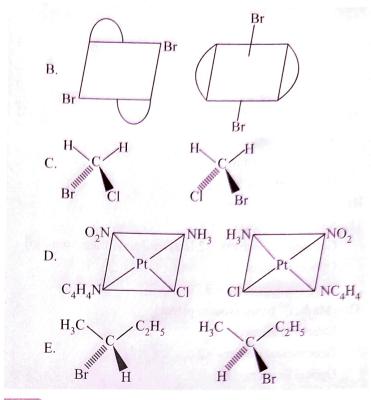




II.Identify the type of isomerism in:

(If no isomerism then indicate none)





#### Sol.

I. Since all atoms in each isomers are attached to the same other types of atoms, the same fragments are expected when the molecules are split.

Therefore ultraviolet (UV), nuclear magnetic resonance (NMR) and X-ray diffraction, conductance method, electrolysis method, chemical method, dipole magnetic and magnetic properties method are used to distinguish isomers.

- II. a. Geometrical isomers are 1 and 3,
  - 4 with 6 and 8
  - 7 with 6 and 8
  - 5 with 6 and 8.
  - **b.** Optical isomers are 6 and 8.
  - c. Identical structures are 1 and 2,
    - 4, 5 and 7.
- III. A. Geometrical isomers
  - B. None
  - C. None
  - **D.** None
  - E. Optical active isomers

#### ILLUSTRATION 7.29

Predict the total number structural and stereoisomers of the following:

- I.  $[Co(NH_3)_5Br]^{2+}$
- II.  $[Ru(H_2O)_4Br_2]^{\oplus}$
- III.  $[Co(en)_2I_2]^{\oplus}$
- **IV.**  $[Ir(py)_2H(Cu)]^{2+}$
- V.  $[Co(Br)(Cl)(en)_2]$
- VI. Na<sub>3</sub>[CoBr<sub>2</sub>(OX)<sub>2</sub>]
- VII. Na<sub>3</sub>[Cr(OX)<sub>3</sub>]
- VIII.  $[Cr(CN)_3(NH_3)_3]$

#### Sol.

- I.  $[Ma_5b]^{n\pm}$  type:
  - Structural isomers = 0
  - Geometrical isomers = 0
  - Optical isomers = 0
- II.  $[Ma_4b_2]^{n\pm}$  type:
  - Structural isomers = 0
  - Geometrical isomers = 2
  - Optical isomers = 0
- III.  $[M(AA)_2b_2]^{n\pm}$  type:
  - Structural isomers = 0
  - Geometrical isomers = 2 [cis  $\Rightarrow d$  and l trans  $\Rightarrow$  meso]
  - Optical isomers = 3
  - Total stereoisomers = 3
- IV. [Ma<sub>2</sub>bc]<sup>n±</sup> types, (square planar)
  - Structural isomers = 0
  - Geometrical isomers = 2
  - Optical isomers = 2
  - Total stereoisomers = 2
- V.  $[M(AA)_2bc]^{n\pm}$  type:
  - Structural isomers = 0
  - Geometrical isomers = 2 ( $cis \Rightarrow d$  and l trans  $\Rightarrow$  meso)
  - Optical isomers = 3
  - Total stereoisomers = 3.
- VI.  $[M(AA)_2b_2]^{n\pm}$  type:
  - Structural isomers = 0
  - Geometrical isomers = 2 ( $cis \Rightarrow d$  and l trans  $\Rightarrow$  meso)
  - Optical isomers = 3
  - Total stereoisomers = 3.
- VII.  $[M(AA)_3]^{n\pm}$  type:
  - Structural isomers = 0
  - Geometrical isomers = 0
  - Optical isomers = 0

#### ILLUSTRATION 7.30

Predict the number of stereoisomers of the following compounds/ions.

- I.  $[CrCl_2(H_2O)(NH_3)_3]$
- II. [Pt FCl(CN)(H<sub>2</sub>O)]<sup>y</sup>
- III. [Pt(gly),]
- IV.  $[Cr(en)(H_2O)_4]^{3+}$

#### Sol.

- I. No. of stereoisomers = 3, cis = 1, trans = 2.
- II. No. of stereoisomers = 3, All geometrical isomers.
- III. No. of stereoisomers = 2, Both are in d and l forms
- IV. No. of stereoisomers = 0.

#### ILLUSTRATION 7.31

Predict the type of isomerism of the following compounds.

I.  $[Cr(CN)(NH_3)_3(en)(C_2O_4)]$  II.  $[Cr(OX)(H_2O)_3(NH_3)] ClO_4^y$ 

**III.** [Zn Cl Br (CN)(NH)<sub>3</sub>]<sup>y</sup> **IV.** [Cr(BrCl)(H<sub>2</sub>O)<sub>4</sub>] [Ag(CN)<sub>2</sub>] **V.** [Cr Br<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>(NH<sub>3</sub>)<sub>2</sub>] Cl

#### Sol.

- I. It can exhibit linkage and geometrical isomerism.
- II. It can exhibit geometrical isomerism. Does not exhibit structural and optical isomerism.
- III. It exhibits optical isomerism
- IV.  $[Cr(BrCl)(H_2O)_4][Ag(CN)_2]$  and

[CrCl(CN)(H<sub>2</sub>O)<sub>4</sub>] [AgBr(CN)] are coordination isomers,

V. It exhibits ionization, geometrical and optical isomerism

**Note:** [Cr Br<sub>2</sub> Cl  $(H_2O)(NH_3)_2$ ],  $H_2O$  is not hydrate isomer of the complex (V)

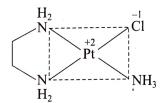
#### ILLUSTRATION 7.32

Predict the number of stereoisomer's of the following compounds/ions.

- I. [PtCl(NH<sub>3</sub>(en)]
- II. [Cr (acac)<sub>3</sub>]
- III.  $Zn(CN)(NH_3)$  (gly)]
- IV. [PdClF(CN(NH,))

#### Sol.

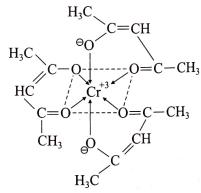
I. It does not exhibit geometrical and optical isomerism because it contains plane of symmetry.

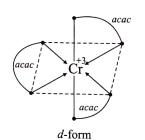


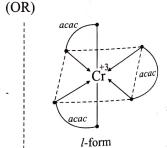
II. It exhibits optical isomerism.

Number of stereoisomers = 2

 $(acac)^{\odot} \Rightarrow$  Acetyl acetonato ion

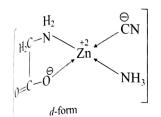






II. It exhibits optical isomerism.

Number of Stereoisomers-2



$$\begin{bmatrix} \ominus & H_2 \\ CN & N-CH_2 \\ Zn & \ominus \\ O-C-O \end{bmatrix}$$

W. Hybridisation of Pd<sup>2+</sup> is dsp<sup>2</sup>. Complex has plane of symmetry hence does not exhibit optical isomerism. But it exhibits geometrical isomerism and number of geometrical isomers = 3.

#### LUSTRATION 7.33

predict the number of stereoisomers of the following compounds/ions.

II. 
$$[CoCl(CN)(en)_2]^{\oplus}$$

$$III. [Cr(en)_3]^{3+}$$

$$\textbf{IV.} \ [\overset{+2}{\text{Cd}}(\overset{-1}{\text{gly}})(\overset{0}{\text{H}_2\text{O}})(\overset{0}{\text{NH}_3})]^{\oplus}$$

$$V[M(en)_2]$$
 VI.  $[M(en) (gly)]$ 

VII. 
$$[M(gly)(NH_3)_2]$$



 $L \Rightarrow 2$  stereoisomers  $(dsp^2)$ 

II.  $\Rightarrow$  3 stereoisomers  $(d^2sp^3)$ 

III.  $\Rightarrow$  2 stereoisomers  $(d^2sp^3)$ 

 $\mathbb{N} \Rightarrow 2$  stereoisomers  $(sp^3)$ 

V., VI. and VII. does not show stereoisomerism. When symmetrical bi-dentate ligand present in coordination number of 4, it does not show stereoisomerism.

#### LUSTRATION 7.34

How many geometrical and stereoisomers are possible for

I. [Mabcd]" and

IL [Mabcdef] $^{n\pm}$  type compounds respectively.



I.  $[Mabcd]^{n\pm}$  type  $\Rightarrow$  3 geometrical isomers no optical isomers.

II. [Mabcdef]<sup> $n\pm$ </sup> type  $\Rightarrow$  15 geometrical isomers and each isomer is optically active.

Total number of stereoisomers for II. = 15 + 15 = 30

## LLUSTRATION 7.35

Predict the number of possible coordination isomers for the following compounds.

 $a_{\text{Cr}(en)_3}$  [Co(OX)<sub>3</sub>]

II.  $[Ni(en)_3][Co(CN)_6]$ 

 $\text{III.} \left[\text{Cu}(\text{H}_2\text{O})_4\right] \left[\text{CuI}_4\right]$ 

I. Total coordination isomers = 4.

 $^{i.} \, [\overset{^{+3}}{Cr} (\overset{0}{en})_3]^{3+} [\overset{^{+3}}{Co} (\overset{^{-6}}{OX})_3]^{3-}$ 

ii.  $[\operatorname{Cr}(OX)(\operatorname{en})_2]^{l+}[\operatorname{Co}(OX)_2(\operatorname{en})]^{l-}$ 

iii.  $[\stackrel{+3}{\text{Co}}\stackrel{-2}{\text{OX}})\stackrel{0}{\text{(en)}}_2]^{l+}[\stackrel{+3}{\text{Cr}}\stackrel{-4}{\text{OX}})_2 \text{ (en)}]^{l-}$ 

iv.  $[Co(en)_3]^{3+}[Cr(OX)_3]^{3-}$ 

II. Total coordination isomers = 4

i.  $[Ni(en)_3]^{3+}[Co(CN)_6]^{3-}$ 

ii.  $[\stackrel{+3}{Ni}\stackrel{-2}{(CN)_2}\stackrel{0}{(en)_2}]^{1+}[\stackrel{+3}{Co}\stackrel{-4}{(CN)_4}\stackrel{0}{(en)}]^{1-}$ 

iii.  $[Co(CN)_2(en)_2]^{1+}[Ni(CN)_4(en)]^{1-}$ 

iv.  $[\overset{+3}{\text{Co}}(\overset{0}{\text{en}})_3]^{3+}[\overset{+3}{\text{Ni}}(\overset{-6}{\text{CN}})_6]^{3-}$ 

III. Total coordination isomers = 2

i.  $[Cu(H_2O)_4]^{2+}[CuI_4]^{2-}$ 

ii.  $[\overset{+2}{\text{Cu}}\overset{-1}{\text{I}}(\overset{0}{\text{H}_2^2\text{O}})_3]^{l+}[\overset{+2}{\text{Cu}}\overset{-3}{\text{I}_3}(\overset{0}{\text{H}_2^2\text{O}})]^{l-}$ 

#### ILLUSTRATION 7.36

If x =Number of cis isomers

y = Number of trans isomers

then calculate  $\frac{x}{y}$  for the complex

+3 -2 -1 -1 -1  $[\operatorname{Cr} \operatorname{Cl}_2 \operatorname{Br} \operatorname{I} \operatorname{F} (\operatorname{CN})]^{-3}$ 

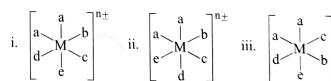
**Sol.** (2) For  $[Ma_2bcde]^{n\pm}$  type:

x = No. of cis isomers = 6

y = No. of trans isomers = 3

$$\therefore \frac{x}{y} = \frac{6}{3} = 2$$

Cis isomers are:



ii. 
$$\begin{bmatrix} a & b \\ e & c \end{bmatrix}^{T}$$

iii. 
$$\begin{bmatrix} a & a \\ d & b \\ e \end{bmatrix}^{n\pm}$$

iv. 
$$\begin{bmatrix} a & b \\ c & e \end{bmatrix}^n$$

iv. 
$$\begin{bmatrix} a & b \\ c & M \\ c & e \end{bmatrix}^{n\pm} \quad v. \quad \begin{bmatrix} a & b \\ e & M \\ e & b \end{bmatrix}^{n\pm} \quad vi. \quad \begin{bmatrix} a & b \\ e & M \\ e & M \\ e & M \end{bmatrix}$$

vi. 
$$\begin{bmatrix} a & a & d \\ e & M & c \end{bmatrix}^{n_2}$$

Trans isomers are:

i. 
$$\begin{bmatrix} b & a & c \\ e & d & d \end{bmatrix}^n$$

ii. 
$$\begin{bmatrix} b & a & d \\ a & c & c \end{bmatrix}^{n\pm}$$

$$i. \begin{bmatrix} b & a & c \\ e & M & d \\ a & a \end{bmatrix}^{n\pm} \quad ii. \begin{bmatrix} b & a & d \\ a & d & c \\ a & a \end{bmatrix}^{n\pm} \quad iii. \begin{bmatrix} b & a & d \\ c & M & e \\ a & a \end{bmatrix}^{n\pm}$$

#### ILLUSTRATION 7.37

Predict the number of geometrical isomers for the complex.

+3 -1 -1 -2  $[\operatorname{Cr} \operatorname{Br} \operatorname{Cl} (\operatorname{gly})_2]^{-1}$ 

#### **Sol.** (6) For [Mab (AB),]<sup>n±</sup> type

(where AB is unsymmetrical bi-dentate ligand e.g.; glycinato:)

$$CH_2 - NH_2$$

$$CH_2 - NH_2$$

$$CH_2 - NH_2$$

No. of geometrical isomers = 6 (2 cis + 4 trans).

#### Cis isomers:

i. 
$$\begin{bmatrix} A & a \\ B & M \\ B & B \end{bmatrix}^{n\pm}$$

ii. 
$$\begin{bmatrix} A & b \\ B & A \end{bmatrix}^{n \pm}$$

#### Trans isomers:

i. 
$$\begin{bmatrix} A & a \\ A & A \\ B & A \end{bmatrix}^{n \pm}$$

ii. 
$$\begin{bmatrix} B & A & b \\ A & A & B \end{bmatrix}^{n\pm}$$

iv. 
$$\begin{bmatrix} A & & & \\ & & & \\ B & & & \\ & & b \end{bmatrix}^{n_{\pm}}$$

#### ILLUSTRATION 7.38

Predict the total number of stereoisomers of the following types of compounds.

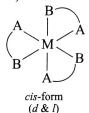
I. 
$$[M(AB)_{1}]^{n\pm}$$

II. 
$$[Ma_2b_2c_2]^{n\pm}$$

III. 
$$[Ma_3b_2c]^{n\pm}$$

#### Sol.

I. No of stereoisomers = 4 (cis and trans & both optically

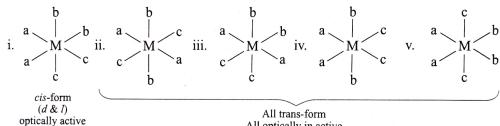


optically active



trans-form (d & l)optically active

II. No. of stereoisomers = 6 (1 cis  $\Rightarrow$  optically active 4 trans  $\Rightarrow$  all optically inactive)

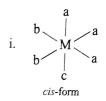


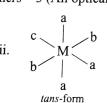
All trans-form All optically in active

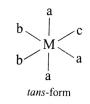
#### **III.** No. of stereoisomers = 3 (All optically inactive).

If x = total number of geometrical isomers in complex:

y = total number of stereoisomers in complex:







# (cis)

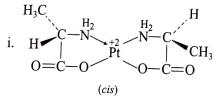
### II. [Cr (acac)<sub>2</sub> Br I]<sup>©</sup>

ILLUSTRATION 7.39

**I.**  $[Pt^{2+}(NH_2 - CH(CH_3) - COO^{\odot})_2]$ 

Then the value of  $\frac{x}{-}$  is

x = No. of Geometrical isomers in (I) = 4 (2 cis + 2 trans)



 $y = \text{No. of stereoisomers in II} = 3 \text{ [1 cis} \Rightarrow \text{optically active},$ 1 trans ⇒ optically inactive]

$$acac^{\odot} = acetylacetonato ion  $\begin{pmatrix} O & O \ominus \\ | & | & | \\ CH_3 - C = CH - C - CH_3 \end{pmatrix}$$$

$$H_3C$$
 $C=O$ 
 $H_3C$ 
 $C=O$ 
 $C=O$ 
 $C=C$ 
 $C=CH$ 
 $CH_3$ 

cis-form (d & 1) optically active

$$\frac{x}{y} = \frac{4}{3} = 1.33$$

## 1.9 MAGNETIC PROPERTIES OF **COORDINATION COMPOUNDS**

The transition metal complexes whose central atom/ion contains me or more unpaired electrons are paramagnetic while those central mmion which have no unpaired electrons (i.e., all electrons are mired) behave as diamagnetic substances. Paramagnetic character acreases with increase in number of unpaired electrons. The paramagnetism of a complex is expressed in terms of magnetic noment  $(\mu)$ . Greater is the number of unpaired electrons in the entral atom/ion of given compound, greater is its paramagnetic the transfer and hence larger is the value of magnetic moment of tecomplex. The magnetic moment is expressed in terms of Bohr Magnetons (BM). Paramagnetic substances have some value of supretic moment whereas diamagnetic substances have zero regnetic moment.

for transition metal complexes,

$$\mu = \mu_l + \mu_s$$

where  $\mu_l$  = orbital magnetic moment, i.e. magnetic moment due to orbital motion of electron.

 $\mu_s$  = spin magnetic moment, i.e. magnetic moment due to spin motion of electron.

$$\mu = \left[\sqrt{l(l+1)} + 2\sqrt{s(s+1)}\right] \frac{eh}{4\pi m}$$
$$= \left[\sqrt{l(l+1)} + 2\sqrt{s(s+1)}\right] B.M.$$

Bohr Magneton.

$$1BM = \frac{eh}{4\pi m}$$

e = charge on electron

h = Plank's constant

m =mass of electron

In case of transition metal ions of 3d-series, the crystal fields the ligands surrounding the metal ions) restrict the movement of the electron around the nucleus in orbitals and hence magnetic moment due to orbital motion of the eletron is quenched ( $\mu_l = 0$ ) and hence  $\sqrt{l(l+1)} = 0$ . Thus magnetic moment of an unpaired electron residing in 3d-orbital of ions of 3d-series is

$$\mu = 2\sqrt{s(s+1)} \text{ BM}$$

$$\therefore \qquad s = \frac{1}{2} \text{ (for one electron)}$$

$$\mu = 2\sqrt{\frac{1}{2} \left(\frac{1}{2} + 1\right)} \text{ BM}$$

For *n* unpaired electrons,  $\mu_{\text{eff}}$  is given as

$$\mu_{\text{eff}} = 2\sqrt{\frac{n}{2}\left(\frac{n}{2}+1\right)} \text{ BM}$$

Since  $\mu_{\text{eff}}$  is only due to the spin motion of n unpaired electrons it is also called spin only magnetic moment and is represented as  $\mu_s$ .

$$\mu_{\text{eff}} = \mu_{\text{s}} = \sqrt{n(n+2)}$$
 BM

The above equation shows that value of  $\mu_{\rm eff}$  depends only on the number of unpaired electrons present in the species.

Greater is the number of unpaired electrons present in orbitals of central metal atom/ion, greater is the value of  $\mu_{\rm eff}$  as shown below:

Number of unpaired electrons	Magnetic moment (μ <sub>s</sub> ) in Bohr magnetons
0	0
1	$\sqrt{3} = 1.73$
2	$\sqrt{8} = 2.83$
3	$\sqrt{15} = 3.83$
4	$\sqrt{24} = 4.90$
5	$\sqrt{35} = 5.92$

#### CONCEPT APPLICATION EXERCISE

#### **Terminology**

- 1. Write the formula of the following compounds according to the IUPAC rule.
  - a. Potassium tetraxoferrate(IV)
  - **b.** Potassium tetrazidocobalt(II)
  - c. Dichloridobis (triphenylphosphine) nickel(II)
  - d. Chloridocarbonylbis (triphenyl phosphine) iridium(I)
  - e. Hexammine cobalt(III) pentachloridocuperate(II)
  - **f.** Tetrammine- $\mu$ -dihydroxobis (ethylenediamine) dicobalt(III) chloride.
  - g. Dibromidotetra ammine cobalt (III) tetrachloridozincate(II)
  - h. Hexammine nickel(II) hexanitrocobaltate(III)
  - i. Hexammine cobalt(III) tetrachloridodiammine chromate(III).
- 2. Name the following compounds:
  - a. [FeCl<sub>2</sub>(H<sub>2</sub>O)<sub>4</sub>]<sup>⊕</sup>
- **b.**  $[Cr(en)_2Cl_2]Cl$
- c.  $[Pt(Py)_{4}][PtCl_{4}]$
- **d.**  $[Co(en)_2(CN)_2]ClO_3$

e. CsTeFs

**f.**  $[Co(NH_3)_5CO_3]_2[CuCl_4]$ 

g. NaMn(CO)<sub>5</sub>

h. (NH<sub>4</sub>)<sub>2</sub>TiCl<sub>6</sub>

i. 
$$\left[ (en)_2 Co \frac{NH}{OH} Co(en)_2 \right]^{3+}$$

j.  $[Cr(acac)_3]$ 

k. [Ni(dmg)<sub>2</sub>]

I.  $SnCl_4$  (Et<sub>2</sub>NH)<sub>2</sub>

3. Give the characteristic coordination number of each of the following central metal ions:

a. Cu(I)

b. Cu(II)

c. Co(III)

d. Al(III)

e. Zn(II) -

f. Fe(II)

g. Fe(III)

h. Ag(I)

4. Indicate the oxidation state of the central metal ion in each of the following complex.

**a.** [Cu(NH<sub>3</sub>)<sub>4</sub>]<sup>2+</sup>

**b.**  $[Cu(Br_4)]^{2-}$ 

c.  $[Cu(CN)_2]^{\Theta}$ 

**d.**  $[Cr(NH_3)_4CO_3]^{\oplus}$ 

e.  $[PtCl_4]^{2-}$ 

f.  $[Co(NH_3)_2(NO_2)_4]^{\Theta}$ 

g. Fe(CO)<sub>5</sub>

h.  $[ZnCl_4]^{2-}$ 

i. [Fe(en)<sub>3</sub>]<sup>2+</sup>

5. Calculate the freezing point of the solution containing 24.8 g solute per kg water for each of the following solutes;  $K_f = 1.86$  °C/m

**a.**  $[Co(NH_3)_3(NO_2)_3]$ 

**b.**  $[Co(NH_3)_4(NO_2)_2][Co(NH_3)_2(NO_2)_4]$ 

c.  $[Co(NH_3)_5(NO_2)][Co(NH_3)_2(NO_2)_4]_2$ [Mw of (a) 248 g (b) 496 g (c) 744 g]

#### Effective Atomic Number (EAN)

6. Calculate EAN in

**a.**  $[Cr(CN)_6]^{3-}$ 

c.  $[Pt(NH_3)_4]^{2+}$ 

b. [PdCl<sub>4</sub>]<sup>2-</sup>
 d. [Cu(CN)<sub>4</sub>]<sup>3-</sup>

7. Calculate "EAN" of metal atoms in the following:

a. Fe(CO)<sub>5</sub>

**b.**  $Co_2(CO)_8$ 

c. Fe(NO)<sub>2</sub>(CO)<sub>3</sub>

**d.**  $Fe(C_5H_5)_2$ 

8. Predict the value of x in each of the following carbonyls:

a.  $Co_2(CO)_r$ 

b. Hx Cr(CO)<sub>5</sub>

c. Hx Co(CO)<sub>4</sub>

d. Mo(CO),

9. (a) If complex compound  $[Fe(\pi - C_5H_5)_x (\pi - C_3H_5)_y]$ (CO) ] is following sidwick's rule of EAN then value of expression "x + y + z" is

**(b)** If complex [Mn (CO),  $(\eta^y - C_5H_5)$ ] follows EAN rule, then value of expression "x + y" is

(c) Calculate the EAN of central metal atom/ion in the following species/compound.

(I) [Co Br I (Trien)]<sup>⊕</sup>

(II) [Ni  $(dmg)_2$ ]

(III)  $[Cr(en)_3]^{3+}$ 

 $(IV) [Ca (EDTA)]^{2-}$ 

(V) [Ni  $(CO)_4$ ]

 $(VI) [Fe (CN)_6]^4$ 

10. (a) EAN of Co (CO)<sub>4</sub> is 35 and hence is less stable. How it attains stability.

(b) Which of the following is an oxidizing agent and

(I) Fe(CO)<sub>o</sub>

(II) Mn(CO)<sub>6</sub>

 $(III) Mn(CO)_5$ 

(IV) Mn<sub>2</sub>(CO)<sub>10</sub>

#### Conductance in Coordination Compounds

11. Arrange the following in order of increasing conductivity in solution.

a. Pt(NH<sub>3</sub>)<sub>6</sub>Cl<sub>4</sub>

b. Cr(NH<sub>1</sub>)<sub>6</sub>Cl<sub>2</sub>

c. Co(NH<sub>3</sub>)<sub>4</sub>Cl<sub>3</sub>

d. K2PtCl6

12. Two compounds have the empirical formula  $Cr(NH_3)_3(NO_3)_3$ In aqueous solution, one of these conducts electricity while the other does not. Deduce their probable structures.

#### Isomerism in Coordiation Compounds

13. How will you distinguish between the following pairs of isomers  $[Cr(NH_3)_3(NO_2)_3]$  and  $[Cr(NH_3)_6][Cr(NO_2)_6]$ .

14. How many geometrical isomers are possible for the complex ion  $[Cr(NH_3)(OH)_2Cl_3]^{2-}$ .

15. The complex M(C<sub>2</sub>O<sub>4</sub>)Cl<sub>2</sub>(NH<sub>3</sub>)<sub>2</sub> forms two types of ionic coloured crystals viz., red (A) and blue (B). Both A and B reacts with 1 mole of AgNO3 to give 1/2 mole of a red precipitate. Further 1 mole of A reacts slowly with 1 mole of Ag<sub>2</sub>C<sub>2</sub>O<sub>4</sub> to form 2 moles of a white precipitate but B does not react with Ag<sub>2</sub>C<sub>2</sub>O<sub>4</sub>. From the above data. Find

a. the coordination number of M

b. the hybrid orbitals of M and

c. stereochemistry of red and blue forms

16. The compound Co(en), (NO<sub>2</sub>), Cl has been prepared in these isomeric forms A, B and C. A does not react with AgNO, or (en) and is optically inactive. B reacts with AgNO, but not with (en) and is optically inactive. C is optically active and reacts with both AgNO3 and (en). Identify each of these isomeric forms and draw their structures.

17. A solution containing 1 g of the complex [Cr(H2O)5Cl]Cl2·H2O was passed through a cation exchanger. The acid liberated was made up to 1 litre. Calculate the strength of acid solution. (Aw of Cr = 52 and Mw of complex =  $266.5 \text{ g mol}^{-1}$ )

18. A solution containing 2.675 g of CoCl<sub>3</sub>·6NH<sub>3</sub> was passed through a cation exchanger. The solution obtained gave 4.305 g of AgCl precipitate with AgNO<sub>3</sub> solution. Determine the formula of the complex.

 $(Mw \text{ of } CoCl_3 \cdot 6NH_3 = 267.5)$ 

## 7.10 BONDING IN COORDINATION COMPOUNDS: VALENCE BOND THEORY (VBT)

The theory was developed by Pauling in 1931. The basic principles involved in this theory are as follows:

a. Orbital hybridisation: The model utilises the hybridisation of s, p and d valence orbitals of central metal atoms of ions (in which electron pairs donated by the ligands are accommodated) to account for observed structures and magnetic properties.

b. Bonding between ligand and the metal atom or ion: From the valence point of view, formation of complex involves reaction between Lewis bases (ligands) and Lewis acids (metal atom/ion) with the formation of coordinate covalent (or dative) bonds between them.

c. Relation between the observed magnetic behaviour and the bond type: That is, the geometry of coordination entity can be predicted of its magnetic behaviour is known.

## 1,10.1 ASSUMPTIONS OF VBT

ed le

- i. The ligands have at least one  $\sigma$ -orbital containing a lone pair of electrons.
- ii. Metal-ligand bond (L→M) arises by the donation of pairs of electrons by ligands to the empty hybridised orbitials of central metal atom or ion. It is basically overlap of atomic orbital of both the entities.
- possess same number of vacant orbitals of equal energy. These orbitals of metal atom (s, p or d) undergo hybridisation to give a set of hybrid orbitals of equal energy and with definite directional properties. These vacant hybrid orbitals now overlap with the ligands to form strong coordinate bonds.
- iv. The non-bonding electrons of the metal occupy the inner orbitals. They are grouped in accordance with Hund's rule. However, under the influence of some strong ligands, there may be some rearrangement of inner electrons in the atomic orbitals (against Hund's rule). During rearrangement generally pairing takes place and consequently some orbitals are vacated and made available for hybridisation.
- v. (For octahedral complexes only) The d-orbitals involved in the hybridisation may be either (n-1) d-orbitals or nd-orbital (n refers to the outermost principle shell of the central metal atom). The complexes formed in two ways are referred to as inner orbital complex (or entity) or outer orbital complex (entity). On the basis of spin they are also referred as low spin and high spin complexes respectively.
- vi. If a complex contain unpaired electrons, it is paramagnetic in nature, whereas if it does not contain unpaired electrons it is diamagnetic in nature.
- vii. Square planar, tetrahedral and octahedral complexes are formed as a result of  $dsp^2$ ,  $sp^3$  and  $d^2sp^3$  (or  $sp^3d^2$ ) hybridisation.

## 7.10.2 Type of Geometry (Structures) OF COMPLEX ENTITIES

In predicting the geometry of complexes, the following points are helpful:

i. Electronic configuration of first transition series:

Atomic number (Z)	Element	Electronic configuration
21	Sc	$3d^1 4s^2$
22	Ti	$3d^2 4s^2$
23	V	$3d^3 4s^2$
24	Cr	$3d^5 4s^1$
25	Mn	$3d^5 4s^2$
26	Fe	$3d^6 4s^2$
27	Co	$3d^7 4s^2$
28	Ni	$3d^{8} 4s^{2}$
29	Cu	$3d^{10} 4s^1$
30	Zn	$3d^{10} 4s^2$

- ii. For coordination number 4, the hybridisations possible are  $sp^3$  and  $dsp^2$ , having tetrahedral and square planar geometries respectively, while for coordination number 6, the hybridisations possible are  $d^2sp^3$  and  $sp^3d^2$  having octahedral geometry in both the cases.
- iii. There are two types of ligands namely strong field and weak field. A strong field ligand is capable of forcing the electrons of the metal atom/ion to pair up (if required). A weak field ligand is incapable of making the electrons of the metal atom/ion to pair up.
- iv. Some ligands have been arranged below from the weakest to the strongest. This arrangement is called spectro chemical series as shown below:

$$\frac{I^{\Theta} < Br^{\Theta} < S^{2-} < SCN^{\Theta} < Cl^{\Theta} < F^{\Theta} < NO_3^{\Theta} < \overset{\Theta}{O}H < urea < EtOH}{Weak field ligand}$$

$$<$$
  $C_2O_4^{2-}$  (OX)  $<$   $O^{2-}$   $<$   $H_2O$   $<$   $NCS^{\Theta}$   $<$  EDTA  $<$   $NH_3$   
Border line field ligands

< NH<sub>3</sub>, pyridine < ethylenediammine (en) < dipyridyl (dipy) < phen < NO<sub>2</sub> 
$$^{\Theta}$$
 < CO

Strong field ligands

#### Note:

- This series has been determined experimentally and is not a postulate of VBT. However, we can use it to predict the structure, electronic configuration, magnetic properties etc. of a coordination complex.
- ii. Ligands given in the borderline criteria act both as strong and weak field ligands. By knowing the value of magnetic moment, it may be suggested that whether they act as a strong and a weak ligand in a particular case.
- iii. Generally NH<sub>3</sub> behaves as a strong field ligand and H<sub>2</sub>O (or ligands nearby it in the series) as a weak field ligand. The compound [Co(OX)<sub>3</sub>]<sup>3-</sup>, is one of the few rare examples where oxalate (OX<sup>2-</sup>) ligand acts as a strong field ligand.

Table 7.16 Some important types of hybridisation and

their geometry						
Coordi-	Types of	Geometry	Examples			
nation	hybridisation	of the				
number		complex				
2	$sp(4s, 4p_x)$	Linear	$K[Ag(CN)_2],$			
_	1		$[Ag(NH_3)_2]^{\oplus}$			
			[CuCl <sub>2</sub> ] <sup>⊖</sup> ,			
			$[Cu(NH_3)_2]^{\oplus}$			
		m ' 1				
3	$sp^2$ (4s, 4 $p_x$ , 4 $p_y$ )	Trigonal	K[HgI <sub>3</sub> ]			
		planar				
4	$dsp^2$	Square	[Ni(CN) <sub>4</sub> ] <sup>2-</sup> , [Pt(NH <sub>3</sub> ) <sub>4</sub> ] <sup>2+</sup>			
	$(3d_{x^2,2}, 4s, 4p_x, 4p_y)$	planar	$[Pt(NH_3)_4]^{2+}$			
			The second of			
4	$sp^2 d$	Square	$[Cu(NH_3)_4]^{2+}$			
,	$(4s, 4p_x, 4p_y, 4d_{x^2-y^2})$	planar	3.4-			
	(x, x, y, x, y, x, y,	1				
4	$sp^3$	Tetrahe-	$[NiCl_4]^{2-}$ ,			
4	$(4s, 4p_x, 4p_y, 4p_z)$	dral	$[Cu(CN)_4]^{3-}$			
	$(43, 4p_x, 4p_y, 1p_z)$	diai	$[Ni(CO)_4]$			
100	, 3	TD: 1				
5.	$dsp^3$	Trigonal	[Fe(CO) <sub>5</sub> ],			
	$(3d_{z^2}, 4s, 4p_x, 4p_y, 4p_z)$		[CuCl <sub>5</sub> ] <sup>3-</sup>			
		dal				
5.	$sp^3d$	Square	$[Sb F_5]^{2-}$			
		pyramidal				
		- 1-4				
6.	$d^2sp^3$	Octahe-	$[Ti(H_2O)_6]^{3+}$ ,			
-	$(3d_{x^2-y^2}, 3d_{z^2}, 4s, 4p_x,$	dral	$[Fe(CN)_{6}]^{3-}$			
	$4p_y$ , $4p_z$ )	(Inner-	$[Fe(CN)_{6}]^{4-}$			
	, -	orbital	$[Co(NH_3)_6]^{3+}$			
		complex)	$[Cr(NH_3)_6]^{3+}$			
6.	$sp^3d$	Octahe-	$[CoF_6]^{3-}$			
	$4s, 4p_x, 4p_y, 4p_z,$	dral	$[Fe(H_2O)_6]^{2+},$			
	$4d_{x^2-y^2}, 4d_{z^2}$	(Outer-	$[Co(H_2O)_6]^{2+}$			
	_	orbital	2 - 761			
		complex)				

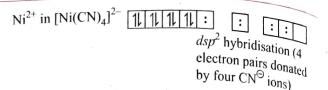
#### 7.10.3 GEOMETRY OF FOUR-COORDINATED **COMPLEXES**

In these complexes, the coordination number of central atom/ion is four. Such complexes may have either square planar or tetrahedral geometry, depending on whether the central atom/ion is  $dsp^2$  or sp<sup>3</sup> hybridised. According to Pauling's prediction, if the complex is paramagnetic it should have tetrahedral geometry, whereas for diamagnetic complex it should be square planar.

Some of the examples are as follows:

1.  $[Ni(CN)_4]^{2-}$  ion: Oxidation state of Ni in  $[Ni(CN)_4]^{2-}$  ion

Ni atom in zero oxidation state/ground state has a configuration of  $3d^8 4s^2$ .



Since the complex is diamagnetic, the two unpaired electrons in 3d, gets paired up making available one vacant 3d orbital One 3d, one 4s and two 4p orbitals hybridise to give  $f_{our}$  $dsp^2$  hybrid orbitals and these orbitals now participate in sigma bond formation with the ligands. Thus  $[[Ni(CN)_4]^2]$ ion has square planar geometry and such no unpaired electron is there, it is diamagnetic.

- i. CN<sup>⊙</sup> being a strong ligand forces pairing of electron to 2-half filled 3d orbitals
- ii. Hybridisation:  $dsp^2$
- iii. Geometry: square planar
- iv. Number of unpaired electrons = 0
- v. Diamagnetic
- vi.  $\mu_s = \text{zero BM}$
- 2.  $[NiCl_4]^{2-}$  ion: This complex ion has  $Ni^{2+}$  ion whose valence shell configuration is  $3d^8 4s^0$ . Magnetic measurements reveal that the given ion is paramagnetic. This is possible only when this ion is formed by  $sp^3$  hybridisation and has tetrahedral geometry.

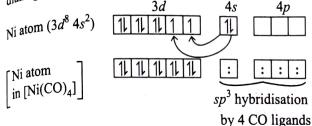
- i.  $Cl^{\Theta}$  is a weak ligand, so no pairing of electrons occurs.
- ii. Hybridisation:  $sp^3$
- iii. Geometry: Tetrahedral
- iv. Number of unpaired electrons = 2
- Paramagnetic
- **vi.**  $\mu_s = \sqrt{2(2+2)} = 2.838 \text{ B.M.}$

#### Note:

- Thus the coordination entities  $[Ni(CN)_4]^{2-}$  and  $[Ni(Cl)_4]^{2-}$ illustrate the useful rule originally called "the magnetic criteria of bond type". That is, the geometry of a coordinated entity can be predicted if its magnetic properties are known. In above case this theory allows prediction of geometry of a four coordinated  $d^8$  complex. If the complex is diamagnetic then its shape will be "square planar" and if it is paramagnetic then its shape will be "tetrahedral".
- ii. The above generalisation of VB theory is not accurate and is one of its draw backs.

Ni(CO)<sub>4</sub>: Oxidation state of Ni in [Ni(CO)<sub>4</sub>] is zero.

Magnetic measurements reveal that the complex is diamagnetic.



Ni in  $[Ni(CO)_4]$  undergoes  $sp^3$  hybridisation and hence  $[Ni(CO)_4]$  has tetrahedral geometry. In this example, paulings's prediction that if the complex is diamagnetic, it should have square planar geometry but it was found to have tetrahedral geometry.

- i. The CO ligand is a strong ligand, so pairing of  $e^{-1}$ 's in 2-half-filled 3d orbitals occurs from 4s orbitals.
- ii. Hybridisation: sp<sup>3</sup>
- iii. Geometry: Tetrahedral
- iv. Diamagnetic
- v.  $\mu_s = \text{zero BM}$
- 4. [Cu(NH<sub>3</sub>)<sub>4</sub>]<sup>2+</sup>: Coordination number of Cu<sup>2+</sup> in [Cu(NH<sub>3</sub>)<sub>4</sub>]<sup>2+</sup> is four. Hence according to VBT, its geometry can be square planar or tetrahedral. Magnetic measurements have predicted this complex to be square planar.

For  $[Cu(NH_3)_4]^{2+}$  to have square planar, Pauling predicted a promotion of an electron from 3d to 4p. Making available one 3d orbital.

$$\begin{bmatrix} \operatorname{Cu}^{2+} \operatorname{atom in} \\ \left[ \operatorname{Cu(NH_3)_4} \right]^{2+} \end{bmatrix} \qquad \underbrace{ \begin{array}{c} 3d \\ \hline 1 \\ \hline 1 \\ \end{array} \begin{array}{c} 4s \\ \hline 1 \\ \end{array} \begin{array}{c} 4p \\ \hline \vdots \\ \end{array} \begin{array}{c} \vdots \\ \hline 1 \\ \end{array} \begin{array}{c} 1 \\ \hline \end{array}$$

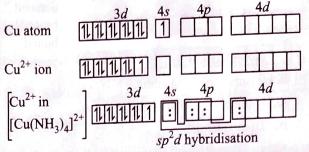
- i. Hybridisation:  $dsp^2$
- ii. Geometry: Square planar
- iii. Number of unpaired electron = 1

iv. 
$$\mu_s = \sqrt{1(1+2)} = \sqrt{3} = 1.732 \text{ BM}$$

If square planar geometry is correct, then the unpaired electron present in higher energy 4p orbital  $(dsp^2)$  hybridisation) should be expected to be easily lost, i.e.  $[Cu(NH_3)_4]^{2+} \xrightarrow{oxidation} [Cu(NH_3)_4]^{3+} + e^{\Theta}$ 

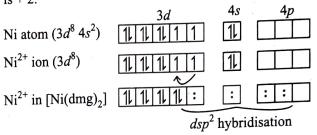
However, experiments have shown that  $[Cu(NH_3)_4]^{2+}$  does not undergo oxidation. This was explained by Huggin.

Huggin suggested that  $[Cu(NH_3)_4]^{2+}$  has square planar geometry, unpair electron in  $Cu^{2+}$  resides in 3*d*-orbital and  $Cu^{2+}$  in  $[Cu(NH_3)_4]^{2+}$  is  $sp^2d$  hybridised as shown below:



Complex ion is paramagnetic with one unpaired electron.

5. [Ni(dmg)<sub>2</sub>] molecule: Oxidation state of Ni in [Ni (dmg)<sub>2</sub>] is + 2.



- i. The (dmg) is a strong ligand so pairing of one electron in 2-half-filled 3d orbitals occurs.
- ii. Hybridisation: dsp<sup>2</sup> iii. Geometry: Square planar
- iv. Number of unpaired electron = zero
- v. Diamagnetic vi.  $\mu_s = \text{zero BM}$
- 6.  $[CoCl_4]^{2-}$ : Oxidation state of Co in  $[CoCl_4]^{2-}$  is + 2.

Co atom $(3d^7 4s^2)$ 1111	3 <i>d</i> 1 1 1 1	4 <i>s</i>	4p
$Co^{2+}$ ion $(3d^7 4s^0)$ 1111			
$Co^{2+}$ in $[CoCl_4]^{2-}$ 1111	1 1 1	$\Box$	::::
	tron pairs	s dona	on (four elected by 4 Cl <sup>©</sup> tetrahedral
	geometry	•	·

- i.  $Cl^{\Theta}$  being weak ligand is unable to force the pairing of electrons.
- ii. Hybridisation:  $sp^3$
- iii. Geometry: Tetrahedral
- iv. Number of unpaired electrons = 3
- v. Paramagnetic

vi. 
$$\mu_s = \sqrt{3(3+2)} = \sqrt{15} = 3.87 \text{ B.M.}$$

7.  $[Zn(NH_3)_4]^{2+}$ : Oxidation state of Zn in complex = +2.

	3 <i>d</i>	<i>4s</i>	4p
Zn atom $(3d^{10} 4s^2)$	1 1 1 1 1	11	
$Zn^{2+}$ ion $(3d^{10})$	11 11 11 11 11		1 124



sp<sup>3</sup> 4 pair of electrons donated by 4NH<sub>3</sub> ligand.

i. Hybridisation:  $sp^3$ 

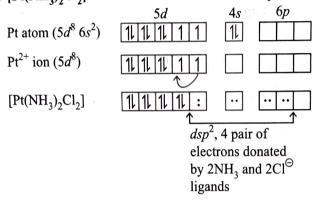
ii. Geometry: Tetrahedral

iii. Number of unpaired electron = 0

iv. Diamagnetic

v.  $\mu_s = \text{zero BM}$ 

8. [Pt(NH<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>]:Oxidation state of Pt in the complex = +2.



i. NH<sub>3</sub> being a strong ligand forces pairing of electrons of 2 half-filled 5*d*-orbitals.

ii. Hybridisation:  $dsp^2$ 

iii. Geometry: Square planar

iv. Number of unpaired electron = 0

iv. Diamagnetic

v.  $\mu_s = \text{zero BM}$ 

#### ILLUSTRATION 7.40

The spin only magnetic moment value of  $[MnBr_4]^{2-}$  ion is 5.9 BM. On the basis of VBT predict the hybridisation and geometry of  $[MnBr_4]^{2-}$  ion.

**Sol.** Oxidation state of Mn is the complex = +2. Since the coordination number of Mn<sup>+2</sup> ion in the complex = 4.

Therefore it will be either tetrahedral  $(sp^3)$  hybridisation or square planar  $(dsp^2)$  hybridisation.

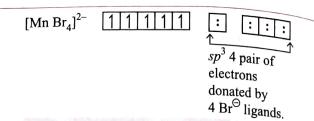
But the fact that the magnetic moment of the complex is 5.9 BM (given), which corresponds to n (number of unpaired electrons) = 5.

Due to the presence of 5 unpaired electrons in the 3d orbitals of  $Mn^{+2}$ , it should be tetrahedral in shape rather than square planar.

If the geometry of the complex ion is tetrahedral

Mn (Z = 25), 
$$\Rightarrow 3d^5 4s^2$$
  
Mn<sup>+2</sup>  $\Rightarrow 3d^5$ 

Since Br<sup>©</sup> is a weak ligand so pairing of electrons in the five half-filled 3d orbitals will not occur.



If the geometry of the complex ion is square planar If the pairing of electrons in the five half-filled 3d orbitals

occurs.  $[MnBr_4]^{2-}$ 

The number of unpaired electron in the complex should be equal to one. So  $\mu_s$  should be equal to  $\sqrt{3} = 3.83$  BM which is not given. Hence hybridisation is not  $dsp^2$  but  $sp^3$ 

#### ILLUSTRATION 7.41

Predict the number of unpaired electrons in square planar [PtCl<sub>4</sub>]<sup>2-</sup> ion.

**Sol.** Oxidation state of Pt in  $[PtCl_4]^{2-}$  ion is +2.  $Pt^{2+}$  is  $5d^8$  ion. For square planar geometry  $dsp^2$  hybridisation is required. For the availability of one d-orbital, pairing of electrons takes place in the remaining d-orbitals. Hence there should be no unpaired electrons in  $[PtCl_4]^{2-}$  ion.

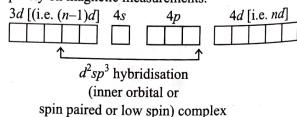
Since  $Cl^{\Theta}$  being weak ligand, so pairing of 3d electrons should not occur, but for square planar complex  $(d sp^2)$  hybridisation, pairing of electrons in 2 half-filled 5d orbitals occurs.

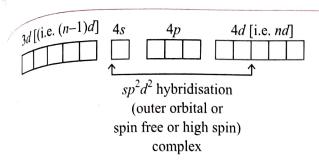
It is a limitation of VB theory.

## 7.10.4 GEOMETRY OF SIX-COORDINATED COMPLEXES

Valence bond theory explains the formation of 6-coordinate octahedral coordination entities by involving the use of (n-1)  $d^2$  ns  $np^3$  or ns  $np^3$  or ns  $np^3$  hybrid orbitals by the central atom/ ion in forming bonds with the ligands i.e. octahedral geometry arises due to  $d^2sp^3$  or  $sp^3d^2$  hybridization of the central atom ion. Octahedral complexes in which the central atom is  $d^2sp^3$  hybridised are called **inner-orbital octahedral complex**, while the octahedral complexes in which the central atom is  $sp^3d^2$  hybridised are called **outer orbital octahedral complexes** as shown below.

This distinction between inner and outer orbital complex is based purely on magnetic measurements.





## 50ME EXAMPLES OF INNER ORBITAL COMPLEXES

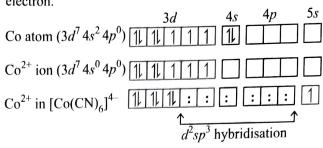
1.  $[Fe(CN)_6]^{3-}$  (hexacyanoferrate(II) ion): Magnetic studies of  $[Fe(CN)_6]^{3-}$  ion has shown that this ion has one unpaired electron and hence paramagnetic.

- i.  $CN^{\Theta}$  being a strong ligand force pairing of 5-half filled 3d orbitals
- ii. Hybridisation:  $d^2sp^3$
- iii. Geometry: Octahedral
- iv. Inner orbital or low spin or spin paired complex.
- v. Number of unpaired electron = 1
- vi. Paramagnetic
- vii.  $\mu_s = \sqrt{3} = 1.732 \text{ BM}$
- 2  $[Fe(CN)_6]^4$  ion (hexacyanoferrate(II) ion): Magnetic studies of  $[Fe(CN)_6]^4$  ion have shown that this complex ion is diamagnetic, i.e. number of unpaired electron on central metal ion is zero (n = 0).

It is due to  $d^2sp^3$  hybridisation that  $[Fe(CN)_6]^4$  is an inner orbital octahedral complex. The electron pair donated by  $CN^{\odot}$  ion (ligand) is accommodated in each of the six  $d^2sp^3$  hybrid orbital as shown above.

- i.  $CN^{\Theta}$  being a strong ligand force pairing of 4 half-filled 3d orbitals
- ii. Hybridisation:  $d^2sp^3$
- iii. Geometry: Octahedral
- iv. Inner orbital or low spin or spin paired complex.
- v. Number of unpaired electron = 0

- vi. Diamagnetic  $\mu_s$  = zero BM
- 3. [Co(CN)<sub>6</sub>]<sup>4</sup> (hexacyanocobalt(II) ion): [Co(CN)<sub>6</sub>]<sup>4</sup> ion is paramagnetic corresponding to the presence of one unpaired electron.



The valence shell electronic configuration of  $\text{Co}^{2^+}$  ion in free state is  $(3d^7 4s^0 4p^0 5s^0)$ , in the complex ion,  $[\text{Co}(\text{CN})_6]^{2^-}$  electronic configuration is  $3d^6 4s^0 4p^0 5s^1$ .

Pauling has suggested that in order to have only one unpaired electron, one electron is forced to pair up in 3*d*-orbital, and remaining one unpaired is promoted to 4*s*.

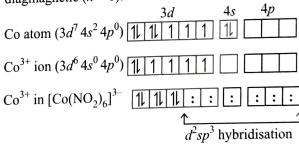
The presence of unpaired electron in 5s is supported by the fact that since 5s orbital is of high energy, the one unpaired electron residing in it should be unstable and hence should be easily lost. Experimentally it has been found to be true.

$$[\text{Co}^{2+}\text{L}_6]^{4-} \longrightarrow [\text{Co}^{3+}\text{L}_6]^{3-} + e^{\Theta}$$

When  $[CoL_6]^{4-}$  is acted upon by air or  $H_2O_2$ , the complex easily gets oxidised to  $[CoL_6]^{3-}$ , thereby losing the unpaired electron present in 5s orbital.

Thus we conclude that  $\mathrm{Co}^{2+}$  inner orbital octahedral complexes are unstable (or labile) and hence gets easily oxidised to  $\mathrm{Co}^{3+}$  complexes by air or  $\mathrm{H_2O_2}$ . Consequently, such complexes should be prepared in an inert atmosphere.

4.  $[Co(NO_2)_6]^{3-}$  (hexanitrito-N-cobaltate(III) ion): Magnetic studies reveal that the given complex is diagmagnetic (n = 0).



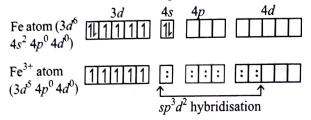
Since the complex is diamagnetic, all the electrons in 3*d*-orbital gets paired up.

- i.  $NO_2^{\Theta}$  being a strong ligand forces pairing of 4 half- filled 3d orbitals.
- ii. Hybridisation:  $d^2sp^3$
- iii. Geometry: Octahedral
- iv. Inner orbital or spin paired or low spin complex.
- $\mathbf{v}$ . Number of unpaired electron = 0
- vi. Diamagnetic
- vii.  $\mu_s = 0$

Note: Oxalate, generally behaves as weak field ligand but with Co(cobalt), it behaves as a strong field ligand like NH3 e.g., in the compound [Co(OX)3]3-.

#### 7.10.5.1 Some Examples of Outer Orbital **Octahedral Complexes**

1.  $[FeF_6]^{3-}$  ion (hexafluoridoferrate(III) ion): In  $[FeF_6]^{3-}$ , CN of Fe is six, hence  $[FeF_6]^{3-}$  ion has octahedral geometry. Oxidation state of Fe in  $[FeF_6]^{3-}$  is +3.



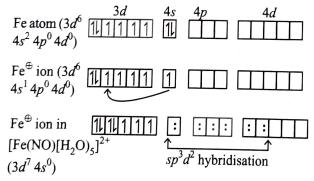
There are five unpaired electrons and hence n = 5. Magnetic properties also reveal that [FeF<sub>6</sub>]<sup>3-</sup> ion is paramagnetic. The two d-orbitals used in  $sp^3d^2$  hybridisation are  $4d_{z^2}$  and  $4d_{x^2-y^2}$  and not  $3d_{z^2}$  and  $3d_{x^2-y^2}$ .

- i.  $F^{\Theta}$  being a weak ligand is unable to pair 5 half-filled 3d
- ii. Hybridisation:  $sp^3d^2$
- iii. Geometry: Octahedral
- iv. Outer orbital or spin free or high spin complex.
- v. Number of unpaired electrons = 5
- vi. Paramagnetic

**vii.** 
$$\mu_s = \sqrt{5(5+2)} = \sqrt{35} = 5.92 \text{ BM}$$

#### 2. $[Fe(NO)(H_2O)_5]^{2+}$ ion (pentaaquanitrosoniumiron(I) ion):

 $[Fe^{\oplus}(NO)^{\oplus}(H_2O)_5]^{2+}$  ion CN of Fe is six, hence it has octahedral geometry. Oxidation state of Fe in  $[Fe(NO) (H_2O)_5]^{2+}$  ion is +1.



- i.  $NO^{\oplus}$  is a strong ligand so forces the pairing of only one unpaired 3s electron to one half-filled orbital of 3d.
- ii. Hybridisation:  $sp^3d^2$
- iii. Geometry: Octahedral
- iv. Outer orbital complex.
- v. Number of unpaired electrons = 3
- vi. Paramagnetic

**vii.** 
$$\mu_s = \sqrt{15} = 3.83 \text{ BM}$$

Note: [Fe(NO)(H<sub>2</sub>O)<sub>5</sub>]<sup>2+</sup> ion is formed in the brown ring test for the confirmation of nitrate ion in the salt analysis. To the nitrate solution, equal volume of freshly prepared saturated solution of FeSO<sub>4</sub> is added. To this solution, conc. H<sub>2</sub>SO<sub>4</sub> is added slowly from the side of the test tube so that acid forms a layer beneath the mixture. A brown ring is formed at the function of the two liquids, due to formation [Fe(NO)(H<sub>2</sub>O)<sub>5</sub>](SO<sub>4</sub>).

$$\begin{aligned} \text{NaNO}_3 + \text{H}_2 \text{SO}_4 &\longrightarrow \text{NaHSO}_4 + \text{HNO}_2 \uparrow \\ 4\text{FeSO}_4 + 2\text{HNO}_2 + 3\text{H}_2 \text{SO}_4 &\longrightarrow 3\text{Fe}_2(\text{SO}_4)_3 + 2\text{NO} + 4\text{H}_2\text{O} \\ \text{FeSO}_4 + \text{NO} + 5\text{H}_2\text{O} &\longrightarrow [\text{Fe}(\text{NO})(\text{H}_2\text{O})_5](\text{SO}_4) \end{aligned}$$

FeSO<sub>4</sub> + NO + 
$$3H_2O \longrightarrow [Fe(NO)(H_2O)_5](SO_4)$$

Brown ring

Ionic equations for NO<sub>3</sub>  $\stackrel{\ominus}{\circ}$  ion test is represented as:
$$[Fe^{+2} \longrightarrow Fe^{+3} + e^{\ominus}] \times 3$$

$$4H^{\oplus} + 3e^{\ominus} + NO_3 \stackrel{\ominus}{\longrightarrow} + NO + 2H_2O$$

$$3Fe^{+2} + NO_3 \stackrel{\ominus}{\longrightarrow} + 4H^{\oplus} \longrightarrow 3Fe^{+3} + NO + 2H_2O$$

$$FeSO_4 \cdot 7H_2O \text{ is represented as } [Fe(H_2O)_6]SO_4 \cdot H_2O$$

$$[Fe(H_2O)_6]^{2^+} + NO \longrightarrow [Fe^{+1} (H_2O)_5 NO^{+1}]^{2^+} + H_2O$$
Brown ring

### 3. [Ni(NH<sub>3</sub>)<sub>6</sub>]<sup>2+</sup> ion (hexaamminenickelate(II) ion:

 $[Ni(NH_3)_6]^{2+}$  ion CN of Ni is six, hence  $[Ni(NH_3)_6]^{2+}$  ion has octahedral geometry. Oxidation state of Ni in [Ni(NH<sub>1</sub>)<sub>c</sub>]<sup>2-</sup> ion is +2.

Note: With most of the central metal/ion, NH3 behaves as a strong ligand but with some metal/ion e.g. Ni<sup>2+</sup> ion, it behaves as a weak ligand.

The above generalisation of V.B. theory is not accurate and is one of its drawbacks.

- In the above complex NH<sub>3</sub> being weak ligand is not able to force pairing of electrons.
- ii. Hybridisation:  $sp^3d^2$
- iii. Geometry: Octahedral
- iv. Outer orbital or spin free or high spin complex.
- v. Number of unpaired electrons = 2
- vi. Paramagnetic

**vii.** 
$$\mu_s = \sqrt{2(2+2)} = \sqrt{8} = 2.83$$
 BM

### 4. [Cr(NH<sub>3</sub>)<sub>6</sub>]<sup>3+</sup> (Hexaaminechromium(III) ion):

Oxidation state of Cr = +3, coordination number (CN) of  $Cr^{3+}$  ion = 6.

Valence electronic configuration of:

Cr atom 
$$\Rightarrow 3d^5 4s^1$$
, Cr<sup>3+</sup> ion =  $3d^3$ 

iv. Number of unpaired electron = 3

v. Paramagnetic

vi. 
$$\mu_s = \sqrt{3(3+2)} = \sqrt{15} = 3.287 \text{ BM}$$

5.  $[C_0F_6]^{3-}$  (Hexafluoridocobaltate(III) ion): Oxidation state of  $C_0 = +3$ , coordination number (CN) of  $C_0^{3+}$  ion = 6.

Valence electronic configuration of:

Co atom  $\Rightarrow 3d^7 4s^2$ , Co<sup>3+</sup> ion =  $3d^6$ .

ii. Hybridisation:  $sp^3d^2$ 

iii. Geometry: Octahedral

iv. Outer orbital or spin free or high spin complex.

Number of unpaired electrons = 4

vi. Paramagnetic

**vii.**  $\mu_s = \sqrt{4(4+2)} = \sqrt{24} = 4.90 \text{ BM}$ 

tible 7.17 Geometry (shape) hybridisation and magnetic nature of some of the complexes (application of valence bond theory)

Atom/ion complex	Configuration	Oxidation state of metal	Hybrid- ization	Geometry (Shape)	No. of unpaired electrons	Magnetic nature
	2	3	4	5	6	7
1						
<b>A</b> $3c^{3+}(d^0)$	3 <i>d</i> 4 <i>s</i> 4 <i>p</i>	+3	_		0	Diamagnetic Diamagnetic
[ScF <sub>6</sub> ] <sup>3—</sup>		+3	$d^2sp^3$ (inner)	Octahedral	0	
za manti	$d^2sp^3$			MgC 12		
В	/	+3	_	_	_	Paramagnetic
Ti <sup>2+</sup> (d <sup>1</sup> ) [TiF <sub>6</sub> ] <sup>3-</sup>	$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	+3	$d^2sp^3$ (inner)	Octahedral	1	Paramagnetic Paramagnetic
Ti(H <sub>2</sub> O) <sub>6</sub> ] <sup>3-</sup>	$\frac{d^2sp^3}{1  \vdots  \vdots  \vdots  \vdots  \vdots  \vdots  \vdots  \vdots  \vdots  $	+3	$d^2sp^3$ (inner)	Octahedral		
$\tilde{d}^{4+}(d^0)$	$\frac{d^2sp^3}{d^2s}$	+4	<del>-</del>	-	0	Diamagnetic Diamagnetic
[TiX <sub>6</sub> ] <sup>2-</sup>		+4	$d^2sp^3$ (inner)	Octahedral	0	

7.56 Inorganic Chem	istry					
C		+3			2	D
$V^{3+}(d^2)$	$\begin{array}{c ccccccccccccccccccccccccccccccccccc$					Paramagnetic Paramagnetic
[V(H <sub>2</sub> O) <sub>6</sub> ] <sup>3+</sup>	$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	+3	$\frac{d^2sp^3}{(inner)}$	Octahedral	2	anagnetic
D						
$\operatorname{Cr}^{3+}(d^3)$	3 <i>d</i> 4 <i>s</i> 4 <i>p</i>	+3	- "	perioral .	3	Paramagnetic
$[Cr(H_2O)_6]^{3+}$		+3	$d^2sp^3$ (inner)	Octahedral	3	Paramagnetic
$\left[\operatorname{Cr(NH_3)_6}\right]^{3+}$	$ \begin{array}{c c}  & d^2sp^3 \\ \hline 1 & 1 & 1 & \vdots \\ \hline  & & & & & \\ \end{array} $	+3	$d^2sp^3$ (inner)	Octahedral	3	Paramagnetic
$\left[\operatorname{Cr(CN)}_{6}\right]^{3-}$	$ \begin{array}{c cccc} \hline d^2sp^3 \\ \hline 1 & 1 & 1 \\ \hline \end{array} $	+3	$d^2sp^3$ (inner)	Octahedral	3	Paramagnetic
$[\operatorname{CrF}_6]^{3-}$	$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	+3	$d^2sp^3$ (inner)	Octahedral	3	Paramagnetic
$[\operatorname{Cr}(\operatorname{NH}_3)_4\operatorname{Cl}_2]^{\oplus}$	$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	+3	$d^2sp^3$ (inner)	Octahedral	3	Paramagnetic
	$d^2sp^3$		1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1			
$\operatorname{Cr}^{\mathrm{o}}(d^{5}s^{1})$	3 <i>d</i> 4 <i>s</i> 4 <i>p</i> 4 <i>d</i>	0	-		5	Paramagnetic
[Cr(CO) <sub>6</sub> ]	$ \begin{array}{c c} \hline 1 & 1 & 1 & \vdots \\ \hline d^2 sp^3 \end{array} $	0	$d^2sp^3$ (inner)	Octahedral	0	Diamagnetic
$\operatorname{Cr}^{2+}(d^4)$	3 <i>d</i> 4 <i>s</i> 4 <i>p</i> 4 <i>d</i>	+2		<u>.</u>	4	Paramagnetic
$[Cr(CN)_6]^4$	1111 ::::::::::::::::::::::::::::::::::	+2	$d^2sp^3$ (inner)	Octahedral	0	Diamagnetic
$\left[\mathrm{Cr}(\mathrm{H_2O})_6\right]^{2^+}$	$ \begin{array}{c cccc}  & d^2sp^3 \\ \hline 1 & 1 & 1 & 1 \\ \hline  & & & & \\ \end{array} $	+2	$sp^3d^2$ (outer)	Octahedral	4	Paramagnetic
$\left[\mathrm{Cr}(\mathrm{NH_3})_6\right]^{2+}$	$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	+2	$sp^3d^2$ (outer)	Octahedral	4	Paramagnetic
E	sp u					
$\frac{\mathbf{E}}{\text{Mn}^{+1} (3d^54s^1)}$	2.4 4 4	. 1			6	Paramagnetic
viii (эи 4s )	$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	+1	_	-		
[Mn(CN) <sub>6</sub> ] <sup>5-</sup>	$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	+1	$d^2sp^3$ (inner)	Octahedral	0	Diamagnetic

					Coordinatio	n Compounds 7.59
VID *2 (3d <sup>5</sup> )	3 <i>d</i> 4 <i>s</i> 4 <i>p</i>	+2	_ '	12 1 - <u>-</u> , 1 ,	5	Paramagnetic
	11111::::::::::::::::::::::::::::::::::	+2	$d^2sp^3$ (inner)	Octahedral	1	Paramagnetic
MnCl <sub>4</sub> l <sup>2-</sup>	$ \begin{array}{c c}  & d^2sp^3 \\ \hline 1 & 1 & 1 & 1 & 1 \\ \hline  & & & & & \\ \end{array} $	+2	$sp^3$	Tetrahedral	5	Paramagnetic
MnBr <sub>4</sub> ] <sup>2-</sup>	sp <sup>3</sup>	+2	$sp^3$	Tetrahedral	5 1	Paramagnetic
$[\mathrm{Mn}(\mathrm{H_2O})_6]^{2^+}$	$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	+2	$sp^3d^2$ (outer)	Octahedral	5	Paramagnetic
1	$sp^3d^2$ $3d   4s   4p$	+3			4	Paramagnetic
$\overline{\mathrm{Mn}^{3^+}(3d^4)}$				tana sala tah		1 3 2 3 1
$[MnF_6]^{3-}$	$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	+3	$sp^3d^2$ (outer)	Octahedral	4	Paramagnetic
	$sp^3d^2$ 3d 4s 4p 4d					_ / 0.2
$[Mn(acac)_3]^0$	$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	+3	$sp^3d^2$ (outer)	Octahedral	4	Paramagnetic
$[Mn(CN)_6]^{3-}$	$\begin{array}{c c} & & & \\ & & & \\ \hline 1 & 1 & \\ \hline \end{array}$	+3	$sp^3d^2$ (inner)	Octahedral	0	Diamagnetic
[MIII(C) 1)61	$\frac{1}{\sqrt{d^2sp^3}}$			- 1 Aug		
<b>F</b> .11	C 1	0			4	Paramagnetic
$Fe(3d^64s^2)$	$\begin{array}{c ccccccccccccccccccccccccccccccccccc$					
Fe(CO) <sub>5</sub>	1111111: : ::::	0	dsp <sup>3</sup> (inner)	Trigonal bipyramidal	0	Diamagnetic
n A . 6 . 1	$\frac{d s p^3}{3d} \qquad 4s \qquad 4p \qquad 4d$	+1			5	Paramagnetic
$Fe^{\oplus} (3d^64s^1)$ $[Fe(H_2O)_5(NO)]^{2^{-1}}$		+1	$sp^3d^2$ (outer)	Octahedral	3	Paramagnetic
[re(H <sub>2</sub> O) <sub>5</sub> (NO)]	$sp^3d^2$		1 1 1 1 1 1 1			
$Fe^{2+}(3d^6)$	3 <i>d</i> 4 <i>s</i> 4 <i>p</i> 4 <i>d</i>	+2	_		4	Paramagnetic
[Fe(NH <sub>3</sub> ) <sub>6</sub> ] <sup>2+</sup>		+2	$sp^3d^2$ (outer)	Octahedral	4	Paramagnetic
[Fe(H <sub>2</sub> O) <sub>6</sub> ] <sup>2+</sup>	$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	+2	$sp^3d^2$ (outer)	Octahedral	4	Paramagnetic
[Fe(CN) <sub>6</sub> ] <sup>4-</sup>	$\begin{array}{c c} & & \\ & sp^3d^2 \\ \hline \hline 11 & 11 & 11 & \vdots & \vdots & \vdots \\ \end{array}$	+2	$d^2sp^3$ (inner)	Octahedral	0	Diamagnetic
0-	$d^2sp^3$		$sp^3$	Tetrahedral	4	Paramagnetic
[FeCl <sub>4</sub> ] <sup>2-</sup>	1111111 : ::::	+2				
	$sp^3$					

## 140.6 LIMITATIONS OF VBT

hile the valence bond theory to a large extent explains the mation, structure and magnetic behaviour of coordination ompounds, it suffers from the following shortcomings:

l. VBT fails to explain the finer details of magnetic

properties including the magnitude of orbital contribution to the magnetic moments, e.g. both tetrahedral (sp hybridisation) and outer orbital octahedral (sp<sup>3</sup>d<sup>2</sup> hybridisation) complexes of Co(+2) ( $d^7$  system) have three unpaired electrons and are therefore expected to have  $\mu_{\rm s}$  = 3.87 BM. The tetrahedral complexes have generally

 $\mu_s$  = value in the range of 4.4–4.8 BM, while the octahedral complexes have  $\mu_s$  in the range of 4.7–5.2 BM VBT cannot explain the increase in value of  $\mu_s$ .

- 2. It does not explain the variation of magnetic properties of complex with temperature.
- 3. The magnetic moment values of complexes of certain ions (e.g. Co<sup>2+</sup>, Ni<sup>2+</sup> etc.) are much higher than those expected by spin only formula. VBT cannot explain the enhanced values of magnetic moment.
- 4. VBT cannot interpret the spectra (color) of the complexes.
- **5.** VBT cannot explain as to why Cu<sup>2+</sup> forms only distorted octahedral complexes even when all the six ligands are identical.
- **6.** It does not make exact predictions regarding the tetrahedral and square planar structures of 4-coordinate complexes.
- 7. It does not give a quantitative interpretation of the thermodynamic or kinetic stabilities of the coordination compounds.
- **8.** It does not explain why in some complexes, metal ion forms inner orbital complex  $(d^2sp^3)$ , low spin complexes) whereas others form outer orbital complexes  $(sp^3d^2)$ , high spin complexes).
- 9. It does not distinguish between strong and weak ligands.

#### ILLUSTRATION 7.42

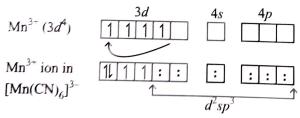
Magnetic moment value of  $[Mn(CN)_6]^{3-}$  ion in 2.8 BM. Predict the type of hybridisation and geometry of the ion.

**Sol.**  $\mu_s = 2.8$  BM corresponds to n = 2.

**Note:** Short method to calculate 'n' (number of unpaired electrons if  $\mu_s$  is given)

Take 2.8 BM  $\approx$  3 B.M., then take its square which is 9 and then take its underroot  $\sqrt{9}$  which is nearly equal to  $\sqrt{8}$  BM when  $\mu_s = \sqrt{8}$  BM, then n = 2.

Thus Mn in  $[Mn(CN)_6]^{3-}$  has two unpaired electrons (n = 2). Oxidation state of Mn in  $[Mn(CN)_6]^{3-}$  is +3, Mn (Z = 25)  $\Rightarrow 3d^54s^2$  and Mn<sup>+3</sup> =  $3d^4$ 



 i. CN<sup>©</sup> being a strong ligand, forces only one pairing of 4 half-filled 3d orbitals.

#### Remember:

- i. In  $d^3$  type electronic configuration, no pairing occurs whether the ligand is strong or weak.
- ii. In  $d^4$  type electronic configuration, only one pairing occurs if the ligand is strong.
- iii. Thus the hybridisation is  $d^2sp^3$  with octahedral geometry.
- iv. Inner orbital complex.

#### ILLUSTRATION 7.43

Magnetic moment value of [Fe(H<sub>2</sub>O)<sub>5</sub>(NO)]<sup>2+</sup> ion in 3.89 B.M. Find out the oxidation state of iron and type of hybridisation.

**Sol.** 
$$\mu_s = 3.89$$
 BM corresponds to  $n = 3$ .

Take 
$$3.89 \approx 4 \Rightarrow \sqrt{16} \approx \sqrt{15}$$
 B.M.

The value  $\sqrt{15}$  BM corresponds to n = 3.

The oxidation state of Fe in the complex.

$$[Fe^{+1}(H_2O)_5^{+1}O]^{2+}$$
 is +1 and CN of  $Fe^{\oplus} = 6$ 

Fe 
$$(Z = 26) \Rightarrow 3d^64s^2$$
, Fe <sup>$\oplus$</sup>  =  $3d^64s^1$ 

Since NO<sup> $\oplus$ </sup> is a strong ligand and H<sub>2</sub>O is a weak ligand so only one pairing of 3d and 4s electrons occurs which also corresponds to n = 3.

$$[Fe^{\oplus}(H_2O)_5NO]^{2+} \underbrace{\begin{array}{c} 3d \\ \hline{1111111111} \\ (n=3) \end{array}}_{sp^3d^2 \text{ hybridisation}} \underbrace{\begin{array}{c} 4s \\ \hline{4p} \\ \hline{4d} \\ \hline{\\ sp^3d^2 \text{ hybridisation}} \\ \end{array}$$

- i. Oxidation state of Fe = +1
- ii. Hybridisation =  $sp^3d^2$
- iii. Geometry = octahedral
- iv. Outer orbital complex.

#### ILLUSTRATION 7.44

In what respects do inner orbital octahedral complexes differ from outer orbital octahedral complexes.

Sol. The differences between inner orbital and outer orbital octahedral complexes have been given in the following table:

Inner orbital octahedral complexes		0	Outer orbital ctahedral complexes
i.	The octahedral hybridisation used in the structure of these complexes involves the use of two $(n-1)$ $d$ , one ns and three $np$ orbitals. In case of $3d$ -block elements this hybridisation is represented as $(3d)^2$ $(4s) (4p)^3$ or simply $d^2sp^3$	ì.	The octahedral hybridisation used in the structure of these complexes involves the use of one ns, three $np$ and two $nd$ orbitals. In case of $3d$ -block elements this hybridisation is represented as $(4s)$ $(4p)^3$ $(4d)^2$ or simply as $sp^3d^2$
	These complexes are given by strong ligands	ii.	These complexes are given by weak ligand

### ILLUSTRATION 7.45

 $\ln [ZnBr_4]^{2-}$  electron pairs in  $sp^3$  hybrid orbitals of the zinc atom form bonds to the bromine atoms. Determine the number of unpaired electrons in the complex.

[ZnBr<sub>4</sub>]<sup>2-</sup> oxidation state of Zn is +2.

Electronic configuration of Zn (Z = 30)  $\Rightarrow 3d^{10}4s^2$ 

$$\Rightarrow Zn^{2+} = 3d^{10}$$

Since the d-orbitals are completely filled, there are no unpaired electrons.

### CONCEPT APPLICATION EXERCISE 7.2

- 1. On the basis of VBT, answer the following complex ions:
  - I. [Ti(bpy)<sub>2</sub>]<sup>⊙</sup>
- **II.**  $[V(H_2O)_6]^{3+}$
- III.  $[Mn(CN)_6]^4$
- **IV.**  $[Mn(CN)_6]^{3-}$
- V.  $[Ir(NH_2)_c]^{3+}$
- a. Type of hybridisation involved.
- b. Type of inner or outer orbital octahedral complex.
- c. Magnetic behaviour and  $\mu_{\rm spin}$  value.
- 2. Identify the complexes which are coloured and which are colourless. Explain.
  - a.  $[Cr(NH_3)_5 (NCS)] [ZnCl_4]$
  - **b.**  $[Ti(NO_3)_4]$
- **c.**  $[Cu(NC-CH_3)_4]^{\oplus} BF_4^{\Theta}$
- **d.**  $[Cr(NH_2)_6]^{3+} 3Cl^{\Theta}$
- e. K<sub>3</sub>[VF<sub>6</sub>]
- 3. Write the IUPAC nomenclature of the given complex along with its hybridisation and structure.
- Ca[Cr(NO) (NH<sub>3</sub>) (CN)<sub>4</sub>],  $\mu_{\rm spin} = 1.73$  BM 4. On the basis of CFT, explain the following complexes of  ${\rm Co}^{3+}$  like  ${\rm [Co(NH_3)_6]}^{3+}$ ,  ${\rm [Co(en)_3]}^{3+}$  and  ${\rm [Co(NO_2)_6]}^{3-}$

- are diamagnetic while  $[CoF_6]^{3-}$  and  $[Co(H_2O)_6]^{3+}$  are paramagnetic.
- 5. Consider the following complex compounds.
  - (I)  $[Pt(NH_3)_4][Pt(NO_2)_4]$
  - (II)  $[Co(H_2O)_6][CoBr_6]$
  - (III)  $[Cr(H_2O)_5 (NO_2)] [Pt (CN)_4]$

If a, b, c are more possible coordination isomers of given complex compounds respectively then calculate the value of a + b + c.

- 6. Consider the following complex compounds.
  - (I)  $[Pt(H_2O)_2(CNS)_2]$
  - (II)  $[Co(CN)_2Br_2]^{2}$
  - (III)  $[Cr(en)_2Cl_2]^{\oplus}$
  - (IV)  $[Cr(NH_3)_3Br_3]$
  - (V)  $[Rh(en)_3]^{3+}$
  - (VI)  $[Pt(en)(CN)_2]$

Calculate the sum total of geometrical isomers in all above compounds.

7. Total number of geometrical isomers of

 $[Pt Br Cl I (CN) (H_2O) (NH_3)]^{2+}$  complex ion, is x and total number of geometrical isomers of the above compound when all the halide ions are in cis position is y then the value of (x + y) is

- **8.** For the complex compound  $[Cu(H_2O)_4]$   $[PtBr_4]$  if x is the number of more coordination isomers and for the compound  $[Cr(gly)(en)_2]^{2+}$  if y is the number of stereoisomers, then (x + y) is
- 9. Total number of complex compound among the following which are optically active?
  - (I)  $[Co(OX)_3]^{3-}$
  - (II)  $[Ru(dipy)_3]^{3+}$
  - (III)  $cis [Cr(NO_2)_3(H_2O)_3]$
  - (IV)  $cis [Cr(CN)_3 (dien)]$
  - (V)  $trans [Cr(CN)_3 (dien)]$
  - (VI)  $cis [Rh Br_{2}(H_{2}O)_{4}]^{\oplus}$
- (VII)  $[Pt(CN)_2(en)]$
- 10. Total number of possible optically active isomers in complex compound (I) and (II) are:
  - (I)  $[Mo Br, I, (gly)]^{-1}$
  - (II) [Cr ClBrI (NH<sub>3</sub>) (en)]
- 11. Find out the total number of optically active isomers for complex compound having molecular formula Pt x (en)Br<sub>4</sub>, where (x = 1, 2, 3)
- 12. The following compounds are given:
  - (I)  $[Pt Cl_4]^{-2}$
  - (II) IF₄<sup>€</sup>
  - (III)  $[Mn (H_2O)_6]^{2+}$
  - (IV)  $IF_7$

If a is the total number of axial d-orbitals having zero nodal plane, b and c are total number of non-axial and axial d-orbitals respectively, each one having two nodal planes used in hybridisation of centrals of compounds I to IV.

Calculate the value of a + b + c.

13. Consider the following transformation

 $Cr(CO)_x \longrightarrow Cr(CO)_y (NO)_z$ 

If both reactant and product follow EAN rule, then calculate the value of x - (y + z).

- 14. Consider the following ligands:
  - (1) acac
- (2) Phen
- (3) DMG
- (4) O<sub>2</sub>
- (5) NO<sub>2</sub>
- (6) NH<sub>2</sub><sup>⊙</sup>
- (7)  $OH^{\odot}$
- (8) Gly
- (9) CO<sub>2</sub><sup>2-</sup>
- (8) Gi
- $(9) CO_3$
- (10) en
- (11)  $SO_4^{2-}$
- (12) CH<sub>3</sub>COO<sup>⊙</sup>

If a = Total number of flexidentate ligands

- b =Total number of ligands which acts as bridging as well as monodentate only
- c = Total number of unsymmetrical bidentate ligands
- d = Total number of bidentate ligands only.

Then calculate the value of (a + b + c - d)

- 15. 100 mL of 0.2 M solution of  $CrBr_3.xNH_3$  was treated with excess of  $AgNO_3$  solution and 0.04 moles of AgBr is precipitated. The value of  $\frac{x}{2}$  is
- 16. Find out the number of compound(s) in which at least half of  $Br^{\Theta}$  ions are ionizable.
  - (I) CoBr<sub>3</sub>.6NH<sub>3</sub>
- (II) CoBr<sub>3</sub>.5NH<sub>3</sub>
- (III) CoBr<sub>3</sub>.4NH<sub>3</sub>
- (IV) CoBr<sub>3</sub>.3NH<sub>3</sub>
- (V)  $PtBr_4.6NH_3$
- (VI) PtBr<sub>4</sub>.5NH<sub>3</sub>
- (VII) PtBr<sub>4</sub>.4NH<sub>3</sub>
- (VIII) PtBr<sub>4</sub>.3NH<sub>3</sub>
- (IX) PtBr<sub>4</sub>.2NH<sub>3</sub>
- 17. Maximum number of N-atom that can lie in molecular plane of the complex [M(trien)]<sup>2+</sup>.
- 18. Find out the total number of ionic species/compounds in which central atom uses  $dz^2$  orbitals in its hybridisation.
  - (I)  $[Cr(H_2O)_6]^{3+}$
- (II) MnO<sub>4</sub><sup>⊙</sup>
- (III) [Pt  $I_2(NH_3)_2$ ]
- (**IV**) Fe (CO)<sub>5</sub>
- (V) [Ni (CNS)<sub>4</sub>]<sup>2-</sup>
- (VI)  $[CrBr_s]^{3-}$
- (VII) Xe<sup>⊖</sup>F,
- (VIII) CIF,
- (IX) Ni (CO)
- 19. Find out the total number of diamagnetic inner orbital complexes.
  - (I)  $[Fe(H_2O)_5NO]SO_4$
- (II) Ca[Fe(CNS),NO]
- (III)  $[Cu(NH_3)_4]S_2O_3$
- (IV) Ca<sub>2</sub>[Co(CNS)<sub>6</sub>]
- (V)  $Na_3[Co(OX)_3]$
- (VI) Ca[NiBr<sub>4</sub>]
- (VII) Na<sub>3</sub>[Fe(CNS)<sub>6</sub>]
- (VIII) Na<sub>3</sub>[Cr(SNC)<sub>6</sub>]
- (IX) Ca[Pt Br<sub>4</sub>]
- 20. If x = maximum number of C-atoms that lie in a plane.
  - y = Number of C-atoms which are  $sp^3$  hybridised.
  - z = Number of C-atoms which are  $sp^2$  hybridised.

Then, find out the value of (x + y - 3) for the complex  $[Ni(dmg)_2]$ 

21. If x = Total number of electron(s) in axial d-orbitals of inner shell of central atom ion in the complex  $[\text{Co(CN)}_6]^3$ 

 $y = \text{Total number of electrons in non-axial } d\text{-orbitals of inner shell of central metal ion in the complex } Co(\text{dmg})_2$ .

22. Consider the following transformation.

$$[\operatorname{Co(H_2O)_x}]^{+3} \xrightarrow{\operatorname{Excess}} [\operatorname{CoCl_y}]^{n-}$$
(Pink complex) Blue complex

Find the value of (x + y - n).

## 7.11 CRYSTAL FIELD THEORY (CFT)

Crystal field theory is now much more widely accepted than the valence bond theory (VBT). This theory was proposed by Bathe and Van Vleck in 1930 and popularised by Orgel in 1952. CFT is an electrostatic model which considers the metal ligand bond ( $M \leftarrow L$ ) to be ionic arising purely from electrostatic interaction between the metal ion and the ligand. Ligands are treated as point charges in case of anions or dipoles in case of neutral molecules which have a lone pair of electrons. If the ligand is a neutral molecule such as  $NH_3$  and  $H_2O$ , the negative end of the dipole in the molecule is directed towards the metal ion. The electrons of the central metal are under repulsive force from those of the ligands. Thus the outermost electrons in the d-orbitals of central transition metal atom/ion occupy those d-orbitals which are far away from the direction of approach of ligands.

In CFT, the following assumptions are made

- 1. Ligands are treated as point charges.
- 2. There is no interaction between metal orbitals and ligand orbitals.
- The arrangement of the ligands around the central metal ion is such that the repulsion between these negative points is minimum.
- 4. Splitting of *d*-orbital energies: The five d-orbitals in an isolated gaseous metal atom/ion, have same energy i.e. they are degenerate (as shown in Fig. 7.28). This degeneracy is maintained if a spherically symmetrical field of negative charges surrounds the metal atom/ion, but all of them will be raised in energy as a result of repulsion between the negative field and the electrons in the orbitals.

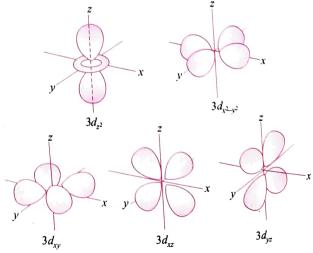


Fig. 7.28 Spatial arrangement of five d-orbitals

However, when this negative field is due to ligands (either anions or the negative ends of dipolar molecules like  $NH_3$ 

and H2O:) in a complex, it becomes asymmetrical and the degeneracy of the d-orbitals is lifted. It results in the splitting of the d-orbitals. The pattern of splitting depends upon the nature of the crystal field. It is this splitting of d-orbital energies and its effects that forms the basis of crystal field theory.

In most transition metal complexes, either six or four ligands surround the metal, giving octahedral or tetrahedral structures. In both of these cases the field produced by the ligands is not spherically symmetrical thus the d-orbitals are not affected equally by the ligand field.

#### 1.11.1 CRYSTAL FIELD SPLITTING OF d-ORBITALS IN OCTAHEDRAL COMPLEXES

i. In an octahedral complex, the metal is at the centre of the octahedron and the ligands are at the six corners. The direction x, y and z point to three adjacent corners of the octahedron as shown in Figure 7.29.

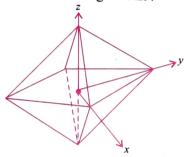


Fig. 7.29 The directions in an octahedral complex

ii. In octahedral coordination entity with six ligands surrounding the metal atom/ion, there will be repulsion between the electrons in the metal d-orbitals and the electrons (or negative charges) of the ligands. Such a repulsion is more when the metal d-orbital is directed towards the ligand than when it is away from the ligand. Thus, the  $d_{x^2-v^2}$  and  $d_{z^2}$ orbitals which point towards the axes along the direction of the ligand will experience more repulsion and will be raised in energy and the  $d_{xy}$ ,  $d_{yz}$  and  $d_{xz}$  orbitals which are directed between the axis will be lowered in energy relative to the average energy in the spherical crystal field (as shown in Figure 7.30).

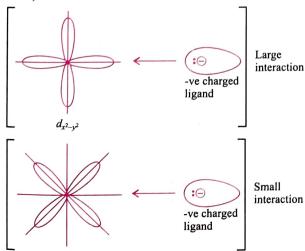


Fig. 7.30 Interaction of ligands with d-orbitals

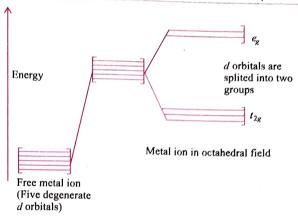


Fig. 7.31 (a) Crystal field splitting of d-orbitals in an octahedral field

Thus, the degeneracy of the d-orbitals have been removed due to ligand electron-metal electron repulsions in the octahedral complex to yield three orbitals of lower energy,  $t_{2g}$  set and two orbitals of higher energy,  $\boldsymbol{e}_g$  set [as shown in Figure 7.31(a) and 7.31(b)].

The lobes of the  $e_g$  orbitals  $(d_{x^2-y^2}$  and  $d_{z^2})$  point along the axes x, y and z. The lobes of the  $t_{2g}$  orbitals  $(d_{xy}, d_{xz})$  and  $d_{yz}$ point in between the axes. It follows that the approach of the six ligands along the x, y, z, -x, -y and -z directions will increase the energy of the orbitals  $d_{\chi^2-\gamma^2}$  and  $d_{z^2}$  (which point along the axes) much more than it increases the energy of the  $d_{xv}$ ,  $d_{xv}$  and  $d_{vz}$  orbitals (which points between the axes).

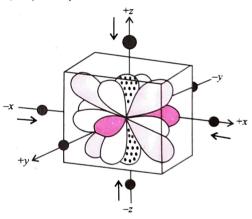


Fig. 7.31 (b) Complete set of d-orbitals in an octahedral produced by six ligands. The  $e_{\sigma}$  orbitals are shaded and the  $t_{2\sigma}$  orbitals are unshaded. The torus of the  $d_{,2}$  orbital has been omitted for clarity

iii. This splitting of the degenerate levels due to the presence of ligands in a definite geometry is termed as crystal field **splitting (CFS)** and the energy separation is denoted by  $\Delta_0$ (the subscript 0 is for octahedral). Thus, the energy of the two  $e_g$  orbitals will increase by  $(\frac{3}{5} \text{ or } 0.6) \Delta_0$  and that of the three  $t_{2g}$  will decrease by  $(\frac{2}{5} \text{ or } 0.4) \Delta_0$ . To understand this splitting more clearly we can assume it be to a two step process as shown in figure.

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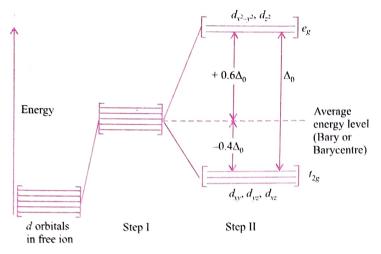


Fig. 7.32 d-orbitals splitting in an octahedral crystal field

**Step 1:** Average energy of the d-orbitals of metal atom/ion in a hypothetical spherical crystal field.

Step 2: Splitting of d-orbitals of metal atom/ion in octahedral crystal field.

In step 1, the ligands approach the central metal, producing a hypothetical spherical field which repels all of the d-orbitals to the same extent. In step 2, the ligands exert an octahedral field, which splits the orbital degeneracy. In going from step 1 to step 2, average energy (the barycentre or "centre ot gravity") of the orbitals must remain constant and thus, the two ' $e_g$ ' orbitals to be further repelled by  $0.6~\Delta_0$  while the three ' $t_{2g}$ ' orbitals are stabilised to an extent of  $0.4~\Delta_0$  as shown in figure 7.32. This constancy of the barycentre of the d-orbitals holds for all complexes, regardless of geometry.

**Note:** The set of *d*-orbitals are divided in two groups:

- i. The orbitals in which lobes lie on the axes  $(d_{x^2-y^2}; d_{z^2})$  referred to as " $e_g$ " orbitals in octahedral symmetry and "e" orbitals in tetrahedral symmetry. (also called as doubly degenerate orbitals). OR where 'e' stands for set of two orbitals and 'g' stands for gerade i.e. symmetrical.
- ii. The orbitals in which lobes lie in between the axes  $(d_{xy}, d_{yx}, d_{zx})$  referred to as " $t_{2g}$ " orbitals in octahedral symmetry and " $t_2$ " orbitals in tetrahedral symmetry (also called triply degenerate orbitals). OR where " $t_{2g}$ " stands for set of three orbitals (t) which are asymmetric with respect to  $C_2$  axis perpendicular to the highest  $C_n$  axis but which is symmetric in sign (g) through the centre of inversion.
- iv. Referring to the energy level of an isolated metal atom, the weighted mean of these two sets of degenerate orbitals is taken as zero, this is some times called the **Barycentre**. The difference in energy between the two d levels is given either of the symbols  $\Delta_0$  or  $10\Delta_a$ .

The size of the energy gap  $\Delta_0$  between the  $t_{2g}$  and  $e_g$  levels can be measured easily by recording the UV-visible spectrum of the complex. Consider a complex like  $[\mathrm{Ti}(\mathrm{H_2O})_6]^{3^+}$ , the  $\mathrm{Ti}^{3^+}$  ion has one d electron. In the complex this will occupy the orbital with the lowest energy, that is one of the  $t_{2g}$  orbitals as shown in Table. The complex absorbs light of the

correct wavelength (energy) to promote the electron from the  $t_{2g}$  level to the  $e_g$  level.

v.  $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$ shows maximum absorption at  $20{,}300$  cm<sup>-1</sup>. The value of  $\Delta_0$  i.e., "Crystal Field Splitting Energy" (CFSE) for  $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$  can be calculated as

$$\Delta_0 = E = \frac{N_{\Lambda}hc}{\lambda} = N_{\Lambda}hc \,\overline{\nu}$$

$$= 6.023 \times 10^{23} \,\text{mol}^{-1} \times 6.6 \times 10^{-34} \,\text{Js} \times 3 \times 10^8 \,\text{ms}^{-1}$$

$$\times 20300 \times 10^2 \,\text{m}^{-1}$$

$$= 242 \,\text{kJ mol}^{-1}$$

Because of the crystal field splitting of *d*-orbitals, the single *d*-electron in  $[\mathrm{Ti}(\mathrm{H_2O})_6]^{3+}$  occupies an energy level 0.4  $\Delta_0$  below the average energy of the *d*-orbitals. As a result the complex is more stable. The crystal field stabilisation energy, CFSE in this case is

CFSE = 
$$-0.4 \Delta_0 = -0.4 \times 242 \text{ kJ mol}^{-1}$$
  
 $\Delta_0 = -96.8 \text{ kJ mol}^{-1}$ 

#### **7.11.2** SIGNIFICANCE OF $\Delta_0$

Consider a  $d^1$  coordination entity e.g.  $[\mathrm{Ti}(\mathrm{H_2O})_6]^{3^+}$  formed in aqueous solution of  $\mathrm{Ti}^{3^+}$  ( $d^1$ ) ion, now the single d-electron occupies one of the lower energy  $t_{2g}$  orbitals. Similarly in the  $d^2$  and  $d^3$  coordination entities, the d-electrons will occupy the lower energy  $t_{2g}$  orbital in accordance with the Hund's rule. For  $d^4$  ions, two possible pattern of electron distribution arise depending upon the relative values of  $\Delta_0$  and P, where P represents the energy required for electron pairing in a single orbital called the **pairing energy**.

- a. If  $\Delta_0 < P$  (weak field, high spin situation): The fourth electron enters one of the  $e_g$  orbitals giving the configuration  $t_{2g}^3 e_g^{-1}$  (see Figure 7.33). If now a fifth electron is added to a weak field coordination entity, the configuration becomes  $t_{2g}^3 e_g^{-2}$ .
- b. If  $\Delta_0 > P$  (strong field, low spin situation): Pairing will occur in the  $t_{2g}$  level with  $e_g$  level remaining unoccupied giving configuration  $t_{2g}^4 e_g^0$ .

**Note:** The pairing will occur (and consequently the  $e_g$  level will remain unoccupied) till the entities of  $d^e$  ions.]

CFSE = 
$$(3 \times -0.4 + 0.6) \Delta_0 = -0.6 \Delta_0$$
  
 $d_{\chi^2-\chi^2}, d_{z^2}$   
 $e_g$   
 $d_{\chi^2-\chi^2}, d_{z^2}$   
 $e_g$   
 $d_{\chi^2} = e_g$ 

Fig. 7.33 Weak field  $\mathrm{CFSE} = [4 \times (-0.4)] = -1.6 \ \Delta_0$ 

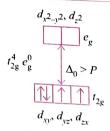


Fig. 7.34 Strong field

**Note:** Calculations show that coordination entities with four to seven *d*-electrons are more stable for strong field as compared to weak field cases.

- c. The CFSE in weak field (Fig. 7.33) is larger than in strong field (Fig. 7.34). However, the energy P used to pair the electrons must be allowed for, so the total stabilisation energy in strong field is  $-1.6 \Delta_0 + P$ .
- d. For a given metal ion P is constant. Thus the amount of CFSE is determined by the strength of the ligand field. A weak ligand (e.g.,  $Cl^{\Theta}$ ) will only cause a small splitting of energy levels  $\Delta_0$ . Thus it will be more favourable energetically for electrons to occupy the upper  $e_g$  level and have a high spin complex, rather than to pair electrons. Similarly, strong field ligands (e.g.  $CN^{\Theta}$ ) cause a large splitting  $\Delta_0$ . In this case it requires less energy to pair the electrons to form a low spin complex.

Similar arguments apply to high and low spin complexes of metal ions with  $d^5$ ,  $d^6$  and  $d^7$  configuration as summarised in Table.

#### 7.11.3 EFFECT OF CRYSTAL FIELD SPLITTING

In octahedral complexes, the filling of  $t_{2g}$  orbitals decreases the energy of a complex that makes it more stable by  $-0.4~\Delta_0$  per electrons.

Filling  $e_g$  orbitals increases the energy by  $+0.6~\Delta_0$  per electron. The total crystal field stabilization energy is given by

$$CFSE_{(octahedral)} = [-0.4n_{(t_{2g})} + 0.6n_{(e_g)}] \Delta_0$$

where  $n_{(t_{2g})}$  and  $n_{(e_g)}$  are the number of electrons occupying the  $t_g$  and  $e_g$  orbitals respectively. The CFSE is zero for ions with  $d^0$  and  $d^{10}$  configurations in both strong and weak ligand fields. The CFSE is also zero for  $d^5$  configurations in a weak field (refer to Table 7.18).

### 7.11.4 FACTORS AFFECTING THE MAGNITUDE OF CRYSTAL FIELD SPLITTING ENERGY

The factors affecting the magnitude of crystal field splitting energy  $(\Delta_0)$  are as follows:

- 1. Nature of the ligands
- 2. Charge on the metal ion
- 3. Size of the metal ion
- 1. Nature of the ligands: Ligands which cause only a small degree of crystal field splitting are termed weak field ligands. Ligands which cause a large splitting are called

strong field ligands. The common ligands can be arranged in increasing order of crystal field splitting  $\Delta_0$ . The order remains practically constant for different metals and this series is called the **spectrochemical series**, which is as follows:

$$\begin{split} & I^{\bigodot} < Br^{\bigodot} < S^{2-} < SCN^{\bigodot} < Cl^{\bigodot} < NO_{3}^{\ \ \bigcirc} < F^{\bigodot} < urea < \stackrel{\bigodot}{O}H < \\ & C_{2}O_{4}^{\ 2-} < O^{2-} < H_{2}O < SCN^{\bigodot} < py, NH_{3} < en < bipy < phen \\ & < NO_{2}^{\ \ \bigcirc} < CN^{\bigodot} < CO \end{split}$$

The series can be split into weak field ligands, border line and strong field ligands. [refer to section 7.10.2, Point (iv)]

The **spectrochemical series** is an experimentally determined series based on the absorption of light. It is difficult to explain the order as it incorporates both the effects of  $\sigma$  and  $\pi$  bonding. The halides are in the order expected from electrostatic effects. In other cases we must consider covalent bonding to explain the order. A pattern of increasing  $\sigma$  donation is follows:

#### Halide donors < O donors < N donors < C donors

The crystal field splitting produced by the strong field  $CN^{\Theta}$  ligand is about double that for weak field ligands like the halide ions. This is attributed to  $\pi$  bonding in which the metal donates electrons from a filled  $t_{2g}$  orbital into a vacant orbital on the ligand. In a similar way, many unsaturated N donors and C donors may also act as  $\pi$  acceptors.

Ligands given in the borderline criteria act as both strong and weak field ligands. By knowing the value of magnetic moment,  $\mu$ , it may be suggested that whether they act as strong and weak in a particular case. Generally, NH<sub>3</sub> behaves as a strong field ligand and H<sub>2</sub>O as weak field ligand. The compound  $[Co(OX)_3]^{3-}$  is one of few rare examples where oxalate ion acts as strong field ligand.

2. Charge on the metal ion: The magnitude of  $\Delta_0$  increases as the charge on the central ion increases.

As the charge on the central atom increases, its interaction with the ligands increases, thereby leading to an increase in value of  $\Delta_0$ .

It has been observed that for the first row transition metal ions, the values of  $\Delta_0$  for  $M^{2+}$  complexes are roughly 50% larger than the values of  $M^{2+}$  complexes.

3. Size of the metal ion: The value of  $\Delta_0$  increases by about 30% between adjacent members down a group of first (3d), second (4d), third (5d) series of transition elements in the order 3d < 4d < 5d.

As the size of the central atom/ion in the complex increases, its interaction with the ligands increases which leads to an increase in the value of  $\Delta_0$ .

## 7.11.5 CFSE AND ELECTRONIC CONFIGURATION IN OCTAHEDRAL COMPLEX

Table 7.18 shows CFSE and electronic arrangement in octahedral complex.

**Table 7.18** CFSE and electronic arrangement in octahedral complex

	complex			The lighter was an experience of the state o
Elec- tronic configu-	Octahedral	n	CFSE $\Delta_0$	Spin only magnetic moment $\mu_s$ (D) =
ration	2007 455 445		TO BE	$\sqrt{n(n+2)}$ BM
$d^1$	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	1	$-0.4 \times 1$ = -0.4	$\sqrt{3} = 1.73$
$d^2$	$\frac{e_{g}}{11-t_{2g}}$	2	$-0.4 \times 2$ = -0.8	$\sqrt{8} = 2.83$
d <sup>3</sup>	$\frac{e_{g}}{111_{t_{2g}}}$	3	$-0.4 \times 3$ $= -1.2$	$\sqrt{15} = 3.87$
d <sup>4</sup>	WF 1_ e <sub>g</sub> 111 t <sub>2g</sub>	4	$-0.4 \times 3$ + 0.6 × 1 = -0.6	$\sqrt{24} = 4.90$
_	SF e <sub>g</sub> 111 t <sub>2g</sub>	2	$-0.4 \times 4$ = -1.6	$\sqrt{8} = 2.83$
d <sup>5</sup>	WF 11 e <sub>g</sub> 111 t <sub>2g</sub>	5	$-0.4 \times 3$ + 0.6 × 2 = -0.0	$\sqrt{35} = 5.92$
	SF e <sub>g</sub> 1 1 1 1 t <sub>2g</sub>	1	$-0.4 \times 5$ $= -2.0$	$\sqrt{3} = 1.73$
d <sup>6</sup>	WF 11 e <sub>g</sub> 111 t <sub>2g</sub>	4	$-0.4 \times 4$ + $0.6 \times 2$ = $-0.4$	$\sqrt{24} = 4.90$
	SF	0	$-0.4 \times 6$ $= -2.4$	0.00
d <sup>7</sup>	WF 11 e <sub>g</sub> 1111 t <sub>2g</sub>	3	$-0.4 \times 5$ + 0.6 × 2 = -0.8	$\sqrt{15} = 3.87$
	SF 1_ e <sub>g</sub> 1111 <sub>t2g</sub>	1	$-0.4 \times 6$ + 0.6 × 1 = -1.8	$\sqrt{3} = 1.73$
	Both WF and SF $11_{e_g}$ $11_{t_{2g}}$		$-0.4 \times 6 + 0.6 \times 2 = -1.2$	$\sqrt{8} = 2.83$

d <sup>9</sup>	Both WF and SF  1 1 e <sub>g</sub> 1 1 1 t <sub>2g</sub>	1	$   \begin{array}{r}     -0.4 \times 6 \\     +0.6 \times 3 \\     =-0.6   \end{array} $	$\sqrt{3} = 1.73$
$d^{10}$	Both WF and SF  1 1 e <sub>g</sub> 1 1 1 t <sub>2g</sub>	0	$-0.4 \times 6 + 0.6 \times 4 = -0.00$	0.00

Note: Symbols used: OH = octahedral complexes,

WF = The configuration for high spin and weak field complexes, SF = The configuration for low spin and strong field <math>complexes, n = Number of unpaired electrons.

#### ILLUSTRATION 7.46

Prove that the lowering of the stabilised orbitals is  $0.4 \Delta_0$  while the raising of the destabilised orbitals is  $0.6 \Delta_0$ .

**Sol.** The total energy of separation is  $\Delta_0$ . Let x = energy of stabilisation and y = energy of destabilisation. Then  $y - x = \Delta_0$ . Since the orbitals yield no net increase in energy when they are equally occupied.

$$\therefore 3x + 2y = 0$$

$$\Rightarrow 3x + 2 (\Delta_0 + x) = 0$$

$$\therefore 5x = -2\Delta_0 \quad x = -0.4 \Delta_0 \text{ and } y = +0.6 \Delta_0$$

## 7.11.6 CFSE OF d-ORBITALS IN TETRAHEDRAL COMPLEXES

A regularly tetrahedron is related to a cube. One atom is at the centre of the cube, and four of the eight corners of the cube are occupied by ligands as shown in Figures 7.35 and 7.36.

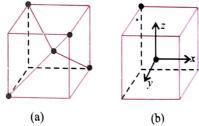


Fig. 7.35 Relation of a tetrahedron to a cube

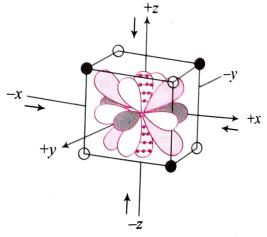


Fig. 7.36 Compete set of d-orbitals in a cubic field. Either set of tetrahedral ligands (● or ○) produces a field one-half as strong as the cubic field

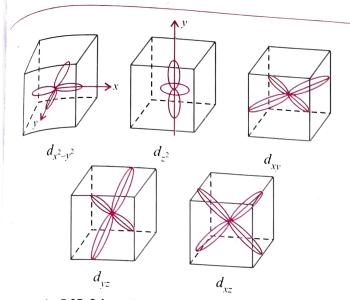


Fig. 7.37 Orientation of a orbitals relative to a cube

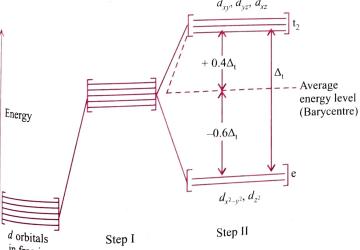
The direction x, y and z point to the centres of the faces of the whe. The orbitals  $d_{xy}$ ,  $d_{xz}$  and  $d_{yz}$  point along x, y and z (that is to the centres of the faces). The orbitals  $d_{x^2-y^2}$  and  $d_{z^2}$  point between  $z_{\text{L}}$  and z (that is towards the centres of the edges of the cube) (as shown in Fig. 7.37).

The ligands do not directly approach any of the metal d-orbitals, but they come closer to the orbitals directed to the edges of the tube  $(d_{xy}, d_{yz})$  and  $d_{xz}$  ) than to those directed to the centres of the cube faces  $(d_{r^2-v^2}$  and  $d_{r^2})$ .

The angle between any of  $d_{xy}$ ,  $d_{yz}$  and  $d_{xz}$  orbital, the central metal and the ligand is half the tetrahedral angle =  $109^{\circ}28'/2$ = 54°44'.

The angle between  $d_{x^2-v^2}$  and  $d_{z^2}$  orbital, the central metal and the ligand is 35°16'.

The approach of the ligands raises the energy of both sets of orbitals. The energy of  $d_{xy}$ ,  $d_{yz}$  and  $d_{xz}$  set of orbitals is raised more because they are closer to the ligands. This crystal field splitting the opposite way round to that in the octahedral complexes as shown in Fig. 7.38.



in free ion Fig. 7.38 d-orbitals splitting in an tetrahedral crystal field

Step I: Average energy of the d-orbitals of metal atom/ion in a hypothetical spherical crystal field.

Step II: Splitting of d-orbitals of metal atom/ion in tetrahedral

Note: In tetrahedral complexes, mostly  $\Delta_t < P(\Delta_t = 4/9 \Delta_0)$  and crystal field. hence they generally form high spin complexes.

Coordination Compounds 7.69 The labels we apply to the two sets of degenerate orbitals are consistent with their symmetry properties in a tetrahedral environment: ' $t_2$ ' for  $d_{xy}$ ,  $d_{yz}$  and  $d_{xz}$  orbitals and 'e' for the  $d_{x^2-y^2}$  and  $d_{z^2}$  orbitals. The 'g' subscript which was used for the octahedral field is no longer appropriate because the tetrahedron lacks a centre of inversion.

The ' $t_2$ ' orbitals are 0.4  $\Delta_t$  above the weighted average energy of the two groups (the Barycentre) and the 'e' orbitals are  $0.6 \Delta_t$ below the average.

The magnitude of the crystal field splitting  $\Delta_t$  in tetrahedral complexes is considerably less than in octahedral field. There are two reasons for this:

- 1. There are only four ligands instead of six, so the ligand field is only two thirds the size, hence the ligand field splitting is also two thirds the size.
- 2. The direction of the orbitals does not coincide with the direction of the ligands. This reduces the crystal field splitting by roughly a further two thirds.

Thus the tetrahedral crystal field splitting  $\Delta_{\rm t}$  is roughly 2/3  $\times$ 2/3 = 4/9 of the octahedral crystal field splitting  $\Delta_0$ . Strong field ligands cause a bigger energy difference between  $t_2$  and 'e' than weak field ligands. However, the tetrahedral splitting  $\Delta_{\rm t}$  is always much smaller than the octahedral splitting  $\Delta_{\rm o}$ . Thus it is never energetically favourable to pair electrons. and almost all tetrahedral complexes are high-spin and low-spin tetrahedral complexes are rarely observed. One such example of low spin tetrahedral complexes of first row transition metal is tetrakis (1-norbornyl) cobalt (IV). Rather, under conditions favouring strong crystal fields. other geometries are preferred over tetrahedral structures.

#### 7.11.7 TOTAL CRYSTAL FIELD STABILISATION **ENERGY**

 $CFSE_{\text{(tetrahedral)}} = [-0.6 \ n_{\text{(e)}} + 0.4 \ n_{\text{(t_2)}}] \ \Delta_t \text{ where } n_{\text{(e)}} \text{ and } n_{\text{(t_2)}} \text{ are the}$ number of electrons occupying the 'e' and ' $t_2$ ' orbitals respectively. The  $\text{CFSE}_{(\text{TH})}$  is zero for ions with  $d^0$ ,  $d^5$  and  $d^{10}$  configuration in both strong and weak ligand field (Refer to Table 7.19).

#### 7.11.8 CFSE IN BOTH OCTAHEDRAL AND **TETRAHEDRAL COMPLEXES**

This shows that for  $d^0$ ,  $d^5$  and  $d^{10}$  arrangements the CFSE is zero in both octahedral and tetrahedral complexes (refer Tables 7.16 and 7.17). For all other electronic arrangements there is some CFSE and the octahedral CFSE is greater than the tetrahedral CFSE. It follows that octahedral complexes are generally more stable and more common than tetrahedral complexes. This is partly because there are six bond energy terms rather than four and partly because there is a larger CFSE term. Despite this some tetrahedral complexes are formed and are stable Tetrahedral complexes are favoured:

- 1. Where the ligands are large and bulky and could cause crowding in an octahedral complex.
- 2. Where attainment of a regular shape is important. For tetrahedral complexes  $d^0$ ,  $d^2$ ,  $d^5$ ,  $d^7$  and  $d^{10}$  configurations are regular. Some tetrahedral complexes which are regular are:

 $\mathsf{Ti}^{\mathsf{IV}}\mathsf{Cl_4}(e^0, t_2^{\ 0}), [\mathsf{Mn}^{\mathsf{VII}}\mathsf{O}_4]^{\Theta}\,(e^0, t_2^{\ 0}), [\mathsf{Fe}^{\mathsf{VI}}\mathsf{O}_4]^{2^-}(e^0, t_2^{\ 0}),$  $[Fe^{III}Cl_4]^{\Theta}(e^2,t_2^{\ 3})\,[Co^{II}Cl_4]^{2-}(e^4,t_2^{\ 3})\,and\,[Zn^{II}Cl_4]^{2-}(e^4,t_2^{\ 6})$ 

- 3. When the ligands are weak field, and the loss in CFSE is thus less important.
- 4. Where the central metal has a low oxidation state. This reduces the magnitude of  $\Delta$ .
- 5. Where the electronic configuration of the central metal is  $d^0$ ,  $d^5$  or  $d^{10}$  as there is no CFSE.
- **6.** Where the loss of CFSE is small, e.g.  $d^1$  and  $d^6$  where the loss in CFSE is 0.27  $\Delta_0$  or  $d^2$  and  $d^7$  where the loss is  $0.53 \Delta_0$ 
  - 7. Many transition metal chlorides, bromides and iodides form tetrahedral structures.

#### 7.11.8.1 Comparison of CFSE and Electronic Arrangement in Tetrahedral (TH) and Octahedral (OH) Complexes

Table 7.19 CFSE and electronic arrangement in TH and OH complexes

Configu- ra- tion		n & μ <sub>spin</sub> BM	CFSE (∆ <sub>t</sub> )	TH (CFSE) scaled for comparison with OH assuming $(\Delta_t) = 4/9\Delta_0$
d¹	1_ e	1 1.73	$-0.6 \times 1$ = -0.6	$-0.6 \times 4/9 \\ = -0.27\Delta_0$
$d^2$	t <sub>2</sub> 11 e	2 2.83	$-0.6 \times 2$ = -1.2	$-1.2 \times 4/9 \\ = -0.53\Delta_0$
$d^3$	1t <sub>2</sub> 11 e	3 3.87	$-0.6 \times 2 + 0.4 = -0.8$	$-0.8 \times 4/9 \\ = -0.36\Delta_0$
d <sup>4</sup>	11 <sub>-t<sub>2</sub></sub> 11 <sub>e</sub>	4 4.90	$-0.6 \times 2 + 0.4 \times 2 = -0.4$	$-0.4 \times 4/9 \\ = -0.18\Delta_0$
d <sup>5</sup>	111 <sub>t<sub>2</sub></sub> 11 e	5 5.92	$-0.6 \times 2 + 0.4 \times 3 = 0.0$	$-0.0 \times 4/9$ = 0.00
d <sup>6</sup>	111 <sub>t2</sub> 11 e	4 4.90	$-0.6 \times 3 + 0.4 \times 3 = -0.6$	$-0.6 \times 4/9 \\ = -0.27\Delta_0$
$d^7$	111 <sub>t2</sub> 11 e	3 3.87	$-0.6 \times 4 + 0.4 \times 3 = -1.2$	$-1.2 \times 4/9 \\ = -0.53\Delta_0$
$d^8$	1111 <sub>t2</sub> 111 e	2 2.83	$-0.6 \times 4 + 0.4 \times 4 = -0.8$	$-0.8 \times 4/9$ = $-0.36\Delta_0$
d <sup>9</sup>	11 11 1 <sub>2</sub> 11 11 e	1 1.73	$-0.6 \times 4 + 0.4 \times 5 = -0.4$	$-0.4 \times 4/9 \\ = -0.18\Delta_0$

$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	0.00	$0.4 \times 6$ $= 0.0$	$-0.0 \times 4/9$ = 0.00
---	------	------------------------	-----------------------------

#### 7.11.9 CFSE OF d-ORBITAL IN SQUARE PLANAR **COMPLEXES**

The square planar geometry may be considered to be derived from octahedral by removing the two ligands which were approaching the central atom along the Z-axis (called tetragonal distortion).

The splitting may also be explained as the lobes of  $d_{x^2-y^2}$  point towards the ligands, this orbital has highest energy.

Though lobes of  $d_{xy}$  orbital lie between the ligands but they are coplanar with them, hence this orbital is next higher in energy, The lobes of  $d_{z^2}$  orbital point out of the plane of the complex but the torus around its centre lies in the plane, therefore  $d_{z^2}$  orbital is next higher in energy. The lobes of  $d_{xz}$  and  $d_{yz}$  orbitals point out of the plane of the complex, hence they are least affected by the electrostatic field of the ligands, and thus have lowest but equal energy. The average energy of the orbitals remains constant in this redistribution of energy as in octahedral and tetrahedral complexes (the stronger the surrounding field, the higher the  $d_{x^2-v^2}$  orbital will be raised, however the lower, occupied orbitals will drop in energy by a corresponding amount) (Fig. 7.39).

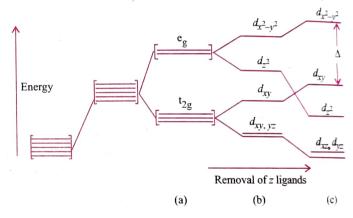


Fig. 7.39 d-orbitals splitting in a square plannar field (a) An octahedral complete undergoing z-axis elongation

(b) It becomes tetragonally distorted and

(c) Finally reaches the square planar limit

**Note:** The  $d_{z^2}$  orbitals may lie below the  $e_{\sigma}(d_{xz}$  and  $d_{zy})$  orbitals in the square planar complex.

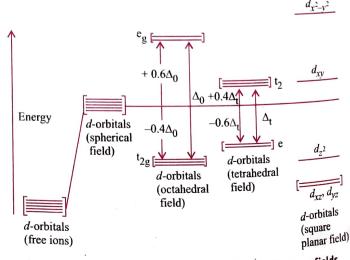


Fig. 7.40 Comparison of crystal field splitting in all three fields

The square planar geometry is favoured by metal ions having a  $d^8$  configuration in the presence of a strong field. This combination The square planar geometry is ravoured by metal ions having a  $d^8$  configuration in the presence of a strong field. This combination plans unoccupied.

# VALUES OF SOME COMPLEXES BY VRT AND CET.

Based on VBT and CFT, the energy level diagram, electronic configuration of the central metal atom/ion and  $\mu_{\rm min}$  values of some of the complexes

$\mu_{\text{spin}}$ values of some of the complexes				
		Electronic configuration		
1.	$[Ni(NH_3)_6]^{2+}$	diagram	No. of unpaired electrons (n) by CFT	μ <sub>spin</sub> (BM)
	strong field ligand	Ni( $Z = 27$ ) = $3d^8 4s^2$		
	CN = 6	$Ni^{2+} = (3d^8) ion = t_{2g}^6 e_g^2$	2	$\sqrt{8} = 2.82$
	Octahedral	25 g 1 1 2		VO - 2.62
	,	3d <sup>8</sup> ion 1 11.11.16		
		$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$		
	2	(VBT) (CFT)		
	$[Cr(CN)_6]^{3-}$	$Cr(Z = 24) = 3d^5 4s^1$		
	strong field ligand	$Cr^{3+} = (2.3)$	3	
	CN = 6 Octahedral	$Cr^{3+} = (3d^3) \text{ ion} = t_{2g}^3 e_g^0$		$\sqrt{15} = 3.87$
- 1	Octanedrai	$\frac{1}{3d^3} \frac{1}{1} \frac$		
		$3d^3$ ion 1 1 1 $t^3$		
		$(n=3) \qquad (n=3)$		
	1 1 2	(VBT) (CFT)		
	$[Mn(CN)_{\epsilon}]^{4}$			
	[Mn(CN) <sub>6</sub> ] <sup>4</sup> -CN <sup>©</sup> strong field	$Mn(Z = 25) = 3d^5 4s^2$	1	F
	ligand, pairing in 't, '	$Mn^{2+} = (3d^5) ion = t_{2g}^5 e_g^0$		$\sqrt{3} = 1.73$
	orbital occurs			
	CN = 6	$ \begin{array}{cccccccccccccccccccccccccccccccccccc$		
	Octahedral	$(n=5) \qquad (n=1)$		
		(VBT) (CFT)		
-	[C <sub>2</sub> (C)D <sub>1</sub> 3-	Many Comments of the Comments		
	[Co(CN) <sub>6</sub> ] <sup>3-</sup>	$Co(Z = 27) = 3d^7 4s^2$	0	0
	strong field ligand, pairing in 't <sub>2g</sub> '	$Co^{3+} = (3d^6) ion = t_{2g}^6 e_g^0$		U
	orbital occurs			
	oronar occurs	$ \begin{array}{cccccccccccccccccccccccccccccccccccc$		
		(n=4) $(n=0)$		
		(N-4) $(N-6)$ $(VBT)$ $(CFT)$		
_		(VBI) (CFI)		
	[lr(NH <sub>3</sub> ) <sub>6</sub> ] <sup>3+</sup>	$Ir(Z = 77) = 5d^7 6s^2$	0	0
	strong field ligand, pairing in	$Ir^{3+} = (5d^6)$ ion = $t_{2g}^6 e_g^0$	· O	0
	't <sub>2g</sub> ' orbital occurs	0		
	Note: High nuclear charge on	1 1 1 1 1 e <sub>g</sub>		
	metal of lower transition (i.e.,	$5d^6$ ion 1 12 12 12 $t_{2g}^6$		
	4d or 5d) series always forms	$(n=4) \qquad (n=0)$		
	low spin inner orbital complex	(VBT) (CFT)		
	irrespective of nature of ligand.			
1	[Fe(CN) <sub>6</sub> ] <sup>4-</sup>	$Fe(Z = 26) = 3d^6 4s^2$	0	0
	strong field ligand	$Fe^{2+} = (3d^6) \text{ ion} = t_{2g}^6 e_g^0$		
	neid ligalid	Fe = (5a) 1011 - 1 <sub>2g</sub> e <sub>g</sub>		
		11111 <sup>1</sup>		
		$3d^6$ ion $1$ 11.11 $t_{2g}$		
		$(n=4) \qquad (n=0)$		
		(VBT) (CFT)		1

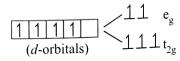
7.	[Fe(H <sub>2</sub> O) <sub>6</sub> ] <sup>2+</sup> weak field ligand	Fe(Z = 26) = $3d^6 4s^2$ Fe <sup>2+</sup> = $(3d^6)$ ion = $t_{2g}^4 e_g^2$	4	$\sqrt{24} = 4.898$
		$ \begin{array}{cccccccccccccccccccccccccccccccccccc$		
8.	$[IrCl_6]^{3-}$ In 3rd transition element series, $\Delta_0$ is so large that it becomes greater than P (pairing energy) $(P < \Delta_0)$ . $Cl^{\Theta}$ acts as strong field ligand and thus pairing of '2g' orbital occurs	$Ir(Z = 77) = 5d^{7} 6s^{2}$ $Ir^{3+} = (5d^{6}) \text{ ion} = t_{2g}^{6} e_{g}^{0}$ $1  1  1  1  1  \dots $	0	0
9.	$[PtCl_6]^{2-}$ Pt is in 5d transition element series, so $(P < \Delta_0)$ $Cl^{\odot}$ is strong field ligand as explained above in point (8)	2g g	0	0
10.	[Rh(NH <sub>3</sub> ) <sub>6</sub> ] <sup>3+</sup> Strong field ligand Rh is in 2nd transition element series	Rh(Z = 45) = $4d^85s^1$ Rh <sup>3+</sup> = $(4d^6)$ ion = $t_{2g}^6 e_g^0$ 1 1 1 1 1 1	0	0
11.	[Mn(CN) <sub>6</sub> ] <sup>3-</sup> Strong field ligand	$Mn(Z = 25) = 3d^{5}4s^{2}$ $Mn^{3+} = (3d^{4}) \text{ ion} = t_{2g}^{4} e_{g}^{0}$ $1 1 1 1 \dots e_{g}^{0}$ $3d^{4} \text{ ion}$ $(n = 4) \text{ (VBT)}$ $(n = 2)$ (CFT)	2	$\sqrt{8} = 2.828$
12.	[CoF <sub>6</sub> ] <sup>4</sup> Weak field ligand	$Co(Z = 25) = 3d^{7}4s^{2}$ $Co^{2+} = (3d^{7}) \text{ ion } = t_{2g}^{5} e_{g}^{2}$ $1  1  1  1  1  e_{g}^{2}$ $(n = 3)  (n = 2)$ $(VBT)  (CFT)$	2	$\sqrt{8} = 2.828$

#### ILLUSTRATION 7.47

For the complex  $[Cr(H_2O)_6]^{2+}$ , calculate the total pairing energy in high spin and low spin state. Given the mean pairing energy  $= 23500 \text{ cm}^{-1}$ .

Sol. In complex  $[Cr(H_2O)_6]^{2^+}$ , oxidation state of Cr is +2, i.e.  $Cr^{2^+}$  is present which has  $3d^4$  configuration. The configuration

of d<sup>4</sup> ion in high spin state is  $t_{2g}^{3} e_{g}^{1}$ , since no electron is paired, total pairing energy of  $[Cr(H_{2}O)_{6}]^{2^{\frac{1}{4}}}$  in high spin state is  $0 \times P = 0$ .  $111111 e_{g}$  (d-orbitals)  $111 t_{2g}$ 



The configuration of d<sup>4</sup> ion in low spin state is  $t_{2g}^{4}$  e<sub>g</sub><sup>0</sup>, since pairing of an electron takes place, total pairing energy of  $\left[Cr(H_{2}O)_{6}\right]^{2^{+}}$  in low spin state is  $1 \times P = 1 \times 23500$  cm<sup>-1</sup> = 23500 cm<sup>-1</sup>.

# ILLUSTRATION 7.48

which complex of the following pairs has the larger value of  $\Delta_0$ . i.  $[\operatorname{Co}(\operatorname{CN})_6]^{3-}$  and  $[\operatorname{Co}(\operatorname{NH}_3)_6]^{3+}$  ii.  $[\operatorname{Co}(\operatorname{H}_2\operatorname{O})_6]^{2+}$  and  $[\operatorname{Co}(\operatorname{H}_2\operatorname{O})_6]^{3+}$  iii.  $[\operatorname{Co}(\operatorname{H}_2\operatorname{O})_6]^{2+}$  and  $[\operatorname{Co}(\operatorname{H}_2\operatorname{O})_6]^{3+}$ 

# i. $[Co(CN)_6]^{3-}$ has larger value of $\Delta_0$ than $[Co(NH_3)_6]^{3+}$ , since $CN^{\Theta}$ has greater field strength than $NH_3$ .

- ii. NH<sub>3</sub> has greater field strength than  $F^{\bigcirc}$  ion, hence  $\Delta_0$  will be greater for  $[Co(NH_3)_6]^{3+}$ .
- iii. Charge on Co in  $[\text{Co(H}_2\text{O})_6]^{2^+}$  is +2, whereas charge on Co in  $[\text{Co(H}_2\text{O})_6]^{3^+}$  is +3. Since charge on  $[\text{Co(NH}_3)_6]^{3^+}$  is higher than  $[\text{Co(NH}_3)_6]^{2^+}$ ,  $\Delta_0$  for  $[\text{Co(NH}_3)_6]^{3^+}$  is larger than  $[Co(NH_3)_6]^{2+}$ .

### ILLUSTRATION 7.49

For Mn<sup>3+</sup> ion, the electron pairing energy, P is 28000 cm<sup>-1</sup>,  $\Delta_0$  values for the complexes  $[Mn(H_2O)_6]^{3+}$  and  $[Mn(CN)_6]^{3-}$  are 21000 cm<sup>-1</sup> and 38500 cm<sup>-1</sup> respectively. Do these complexes have high spin or low spin complexes? Also write the configurations corresponding to these states.

Sol. For  $[Mn(H_2O)_6]^{3+}$  ion,  $\Delta_0 < P(\Delta_0 = 21000 \text{ cm}^{-1}, P = 28000 \text{ cm}^{-1})$ . Hence this is a high spin complex (pairing up of electron will not take place). Mn in  $[Mn(H<sub>2</sub>O)<sub>6</sub>]^{3+}$  is present as  $Mn^{3+}$  ion.  $\text{Mn}^3$  ion is  $d^4$  system, its configuration is  $t_{2g}^{-3}$   $e_g^{-1}$ .

For  $[Mn(CN)_6]^{3-}$  ion  $\Delta_0 > P (\Delta_0 = 38500 \text{ cm}^{-1}, P = 38500 \text{ cm}^{-1})$ 28500 cm<sup>-1</sup>). Hence pairing of electron will take place and the  $[Mn(CN)_6]^{3-}$  is low spin complex. Mn in  $[Mn(CN)_6]^{3-}$  is present as  $Mn^{3+}$  ion which is  $d^4$  system, its configuration is  $t_{2g}^{4} e_{g}^{0}$ 

## ILLUSTRATION 7.50

For  $[Cr(H_2O)_6]^{2+}$  ion, the mean pairing energy P is found to be 23500 cm $^{-1}$ . The magnitude of  $\Delta_0$  is 13900 cm $^{-1}$ . Calculate the crystal field stabilisation energy for the complex in configurations corresponding to high spin and low spin states. Which is more stable?

Sol. In  $[Cr(H_2O)_6]^{2+}$  ion, Cr is present as  $Cr^{2+}$  ion. Electronic configuration of  $Cr^{2+}$  ion is  $3d^4$ ,  $Cr^{2+}$  ion in high spin states:  $t_{2g}^{\phantom{2g}} c_g^{\phantom{2g}}$ .

CFSE = 
$$-3 \times 0.4 \Delta_0 + 1 \times 0.6 \Delta_0$$
  
=  $-1.2 + 0.6 \Delta_0 = -0.6 \Delta_0 = -0.6 \times 13900 \text{ cm}^{-1}$   
=  $-8340 \text{ cm}^{-1}$ 

 $Cr^{2+}$  ion in low spin state:  $t_{2g}^{4} e_{g}^{0}$ 

CFSE = 
$$-4 \times 0.4 \Delta_0 + P$$
  
=  $-(1.6 \times 13900 + 23500) \text{ cm}^{-1}$   
=  $(-22240 + 23500) \text{ cm}^{-1} = +1260 \text{ cm}^{-1}$ 

CFSE for high spin state is greater than CFSE for low spin state,

hence high spin state is more stable.

## ILLUSTRATION 7.51

Give reason for the fact that crystal field theory is not applied to complexes of many group metals.

Sol. Main group metals do not have incomplete d subshells, rather they have empty or completely filled d subshells. For empty or completely field d-subshells,  $\Delta = 0$ , hence crystal field theory is not applied to complexes of main group metals.

### ILLUSTRATION 7.52

- a. Using CFT, depict the electronic configuration of the rhodium ion (Rh2+) in an octahedral field for which the crystal field splitting  $\Delta_0$  is greater than the pairing energy P.
- **b.** Calculate the crystal field stabilisation energy for this configuration (in terms of  $\Delta$  and P)

### Sol.

**a.** Rh  $(Z = 45) \Rightarrow 4d^8 5s^1$ , Rh<sup>2+</sup> =  $4d^7$ 

 $Rh^{2+}$  ion in octahedral field has configuration  $t_{2g}^{\phantom{2}6}\,e_{g}^{\phantom{2}1}$  when crystal field splitting  $\Delta_0$  is greater than the pairing energy P.

**b.** For Rh<sup>2+</sup> ion, in octahedral field  $(\Delta_0 > P)$ .

CFSE = 
$$-(0.4 \times 6) \Delta_0 + (0.6 \times 1) \Delta_0 + P$$
  
=  $-2.4 \Delta_0 + 0.6 \Delta_0 + P = -1.8 \Delta_0 + P$ 

(Even in a spherical field, the complex must have two pairs of electrons, one additional pair is formed in the octahedral field)

### ILLUSTRATION 7.53

What factor determines whether the crystal field in an octahedral complex is to be regarded as strong or weak? How many d-electrons must be present in orbitals of the central atom for there to be an abrupt change in crystal field stabilisation energy between strong and weak fields?

Sol. Crystal field in an octahedral complex, to be regarded as strong or weak, depends on the relative magnitude of  $\Delta_0$  and P.

- **a.** If  $\Delta_0 > P$ , Strong field
- **b.** If  $\Delta_0 \le P$ , Weak field

Abrupt changes in crystal field stabilisation energy between strong and weak fields occur with  $d^4$ ,  $d^5$ ,  $d^6$  and  $d^7$  configurations.

### 7.11.11 APPLICATIONS OF CFT

Crystal field theory (CFT) is successful in explaining:

- i. Stability of the different stereochemical arrangements observed in different complexes.
- ii. Spectral properties of complexes involving d-d transition.
- iii. Distortion from the symmetrical geometries with certain
- iv. Magnetic properties of coordination compounds.

# 7.11.12 LIMITATIONS OF CFT

Crystal field theory is not very clear about the following:

- i. The spectrochemical series: CFT assumes the interaction between central metal atom/ion and ligands in the complex to be electrostatic and therefore the anionic ligands should give maximum crystal field splitting. The reverse has been found to be true, i.e. halides  $(X^{\Theta})$  are at the bottom of spectrochemical series (weak field ligands), <sup>9</sup>OH, a strong base gives a field which is weaker than H2O (neutral ligand and have a larger size).
- ii. The radial wave functions of the d-orbitals and of the ligands should have some overlap at the observed internuclear distances in the metal complexes. The ligands therefore are not point charges, but have their own electron orbitals.
- iii. The CFT cannot account for the  $\pi$ -bonding in the complexes.
- iv. CFT cannot explain the charge transfer spectra and the intensities of the absorption bands. These are some of the limitations of CFT, which are explained by ligand field theory (LFT).

# 7.12 JAHN-TELLER EFFECT AND **DISTORTION IN OCTAHEDRAL** AND TETRAHEDRAL COMPLEXES

# Distorted Octahedral Complexes

In an octahedral complex all the six M-L (L= ligand and M=central metal atom) bond lengths are equivalent. If M-L bonds are of unequal lengths, the octahedral geometry of the complex gets distorted and we get distorted octahedral complex.

# 7.12.1 Types of Distorted Octahedral COMPLEXES

- 1. Tetragonally elongated distorted octahedral complexes: (Also see Fig. 7.41). These complexes are also called simply by the name tetragonally distorted octahedral complexes. In an octahedral complex, if the two trans or axial ligands (L<sub>2</sub>) are moved away from the central metal atom, the distances of these two ligands from the metal atom becomes larger than that of each of the remaining four coplanar equatorial ligands (L<sub>o</sub>) from the central metal atom. Thus the two trans bonds (also called axial bonds) or metal-ligand bonds along +z and -z axes become longer than each of the four equatorial bonds (equatorial) bonds are metal-ligand bonds along +x, -x, +yand -y axes in xy plane. The trans bonds become longer because these bonds are weaker than the equatorial bonds. Such octahedral complexes in which the two trans ligands are longer than each of the four equatorial bonds are called tetragonally elongated distorted octahedral complexes or simply tetragonally distorted octahedral complexes (See Fig. 7.41). The distortion which gives tetragonally distorted octahedral complex is called tetragonal elongation distortion.
- 2. Square planar complexes: (Also see Fig. 7.41). Some times the tetragonal elongation distortion in tetragonally elongated octahedral complexes is so large that the two trans ligands on z-axis are completely removed and hence octahedral complex adopt square planar geometry. For example square

planar complexes of Cu(II) are highly distorted octahedral

3. Tetragonally compressed distorted octahedral complexes, (Also see Fig. 7.41). In an octahedral complex, if the  $t_{W0}$ trans ligands are brought nearer to the central metal atom, the distance of these two trans ligands from the metal atom, becomes shorter than that of each of the remaining four equatorial ligands from the central metal atom. Thus the two trans ligands become shorter than each of the four equatorial bonds. The two trans ligands become shorter because these bonds are stronger than the equatorial bonds. Such octahedral complexes in which the two trans ligands are shorter than each of the four equatorial bonds are called tetragonally compressed (or contracted) distorted octahedral complexes. The distortion which gives tetragonally compressed distorted octahedral complex is called tetragonal contraction distortion.

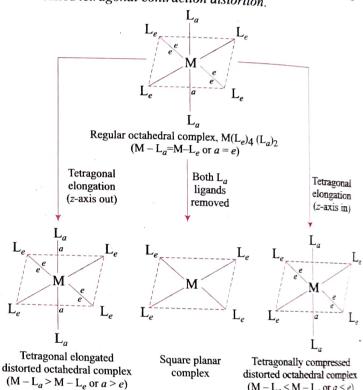


Fig. 7.41 Different types of distorted octahedral complexes

 $(M - L_a \le M - L_e \text{ or } a \le e)$ 

4. Trigonally distorted octahedral complexes: Trigonal prismatic complexes: When an axis passing through the centres of the two opposite triangular faces of an octahedron is increased (elongation) or decreased (compression or contraction) in length, octahedral complex gets distorted and assumes trigonal prismatic geometry (See Fig. 7.42).

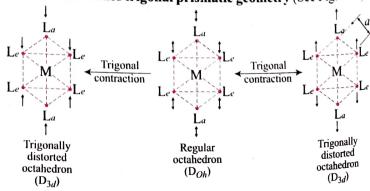


Fig. 7.42 Trigonal distortion in an octahedral ML<sub>6</sub> complex

# 112.2 TYPES OF DISTORTION IN OCTAHEDRAL **COMPLEXES**

forgoing discussion clearly shows that the octahedral complexes can undergo the following types of distortion.

(i) Tetragonal distortion. This distortion is of the following two types:

- (a) Tetragonal elongation distortion
- (b) Tetragonal contraction (or compression) distortion.
- (ii) Trigonal distortion
- (iii) Rhombic distortion.

# 1,12.2.1 Symmetrically and Asymmetrically (Unsymmetrically) Filled $t_{2g}$ and $e_g$ Sets of

If  $l_{2g}$  set of orbitals (i.e.,  $d_{xy}$ ,  $d_{yz}$  and  $d_{zx}$  orbitals) contains 0 (empty, § 3 (half-filled,  $t_{2g}^3$ ) or 6 (completely-filled,  $t_{2g}^6$ ) electrons, the anangement (distribution) of these electrons in this set is said be symmetrical arrangement and  $t_{2g}$  set of orbitals is said to be symmetrically-filled. On the other hand, if  $t_{2g}$  set contain 1, 2.4 or 5 electrons, the arrangement of these electrons is said to asymmetrical arrangement and  $t_{2g}$  set of orbitals is said to be asymmetrically filled. Thus:

- (i)  $t_{2g}^0$  (empty),  $t_{2g}^3$  (half-filled),  $t_{2g}^6$  (completely-filled)... symmetrically filled orbitals.
- (ii)  $t_{2\sigma}^1, t_{2\sigma}^2, t_{2\sigma}^4, t_{2\sigma}^5, \dots$  asymmetrically-filled orbitals.

If  $e_g$  set of orbitals (i.e.,  $d_{x^2-y^2}$  and  $d_{z^2}$  orbitals) has zero (empty,  $e_g^0$ ), 2 (half-filled  $e_g^2$ ) or 4 (completely filled,  $e_g^4$ ) electrons, the arrangement of these electrons in this set is said to be symmetrical arrangement and  $\boldsymbol{e}_{\mathrm{g}}$  set of orbitals is said to be symmetrically filled. On the other hand, if  $e_g$  set has 1 or 3 electrons, this arrangement of electrons is said to be asymmetrical arrangement of electrons and  $e_g$  set is said to be a symmetrically filled. Thus:

- (i)  $e_g^0$  (empty),  $e_g^2$  (half-filled),  $e_g^4$  (completely filled) ... symmetrically filled orbitals
- (ii)  $e_{\alpha}^{1}$ ,  $e_{\alpha}^{2}$  ... asymmetrically-filled orbitals.

Note: We know that  $d^3$  ion is represented by the configuration,  $t_{2g}^b, e_g^2$  in LS octahedral complexes. In this configuration, both the electrons of  $e_g$  set are assumed to be present in  $d_{z^2}$  orbital and  $d_{x^2-y^2}$  orbital remains vacant. Thus  $t_{2g}^6 e_g^2$  configuration is represented as  $t_{2g}^6 d_{z^2}^2 d_{x^2-y^2}^0$ . In this configuration, although  $e_g$ set is half-filled, it is said to asymmetrically filled, since both the electrons are in  $d_2$  orbital.

# 7.12.2.2 Jahn-Teller Theorem or Jahn-Teller Effect

In 1937, Jahn and Teller put forward a remarkable theorem to explain why some six coordinated complexes (octahedral complexes) undergo distortion and have distorted octahedral geometry. This theorem states that if a molecule / complex Possessing any shape (excepting linear shape) has an unsymmetrically filled set of degenerate orbitals is unstable and hence undergoes distortion. This distortion takes place

in such a way that the symmetry and energy of the molecule / complex is lowered and hence the molecule / complex becomes more stable. This theorem does not say which type of distortion will occur in the molecule / complex. Thus, according to this theorem, if the electrons in d-orbitals of the central metal ion of a regular octahedral complex are asymmetrically arranged, the octahedral shape of the complex will get distorted, since the electrons present in a symmetrically-filled d-orbitals will repell some ligands to greater extent while other ligands will be repelled to lesser extent. The distortion in geometry of non-linear system due to Jahn-Teller effect is called Jahn-Teller distortion.

# 7.12.3 DISTORTION SHOWN BY OCTAHEDRAL COMPLEXES OF dx lons (x = 0 to 10)

Octahedral complexes of some  $d^x$  ions show strong distortion while some ions show weak distortion. There are also some ions which do not show any distortion.

- 1.  $d^0$  ion  $(t_{2g}^0 e_g^0$  with n = 0): Octahedral complexes of  $d^0$  ion do not show any distortion. Examples of such complexes are  $[TiX_6]^{2-}$  where X = F, Cl.
- 2.  $d^1$  ion.  $Ti^{3+}$  ion is a  $d^1$  ion: This ion is present in octahedral complex ion,  $[Ti(H_2O)_6]^{3+}$ . In the ground state  $d^1$  configuration is represented as  $t_{2g}^1 e_g^0$ ,  $t_{2g}^1$  electron may be present in  $d_{xy}$  orbital  $d_{xz}/d_{yz}$  orbital. When  $t_{2g}^1$  electron is present in  $d_{xy}$  orbital,  $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$  ion undergoes strong distortion and assumes compressed distorted octahedral geometry. On the other hand, if  $t_{2g}^1$  electron is present in  $d_{xz}$  or  $d_{yz}$  orbital,  $[\mathrm{Ti}(\mathrm{H_2O})_6]^{3+}$  undergoes strong distortion and assumes elongated distorted octahedral geometry.
  - 3.  $d^2$  ion: E.C. of  $d^2$  ion is  $t_{2g}^2 e_g^0$  (n = 2). This configuration has asymmetrically filled  $t_{2g}$  orbitals and empty  $e_g$  orbitals. Hence octahedral complexes of  $d^2$  ion show slight distortion.
  - **4.**  $d^3$  ion: E.C. of  $d^3$  ion is  $t_{2g}^3 e_g^0$  (n=3). In this configuration  $t_{2g}$  orbitals are symmetrically filled and  $e_g$  orbitals are empty. Octahedral complexes of  $d^3$  ion, therefore, do not show any distortion (no distortion). Examples of such complexes are  $[Cr(ox)_3]^{2-}$ ,  $[Cr(H_2O)_6]^{+3}$  etc.
  - 5. (a)  $d^4$ (HS) ion:  $Cr^{2+}$  and  $Mn^{3+}$  ions are  $d^4$  ions. Since the configuration of weak field (HS) 6-coordinated complexes of these ions viz  $t_{2g}^3 e_g^1$  has asymmetrically-filled  $e_g$  set, these complexes show strong distortion in their octahedral shape. One electron present in  $e_{\rm g}$  set may be present either in  $d_{z^2}$  orbital or in  $d_{x^2-y^2}$  orbital. If the single electron is supposed to be present in  $d_{x^2-v^2}$  orbital, this electron is repelled by four ligands lying on +x, -x and +y and -yaxes. On the other hand, if the single electron is assumed to be present in orbital, this electron is repelled by two ligands lying on +z and -z axes. Thus the energy of  $d_{x^2-y^2}$ orbital increases relative to  $d_{z^2}$  orbital. This leaves  $d_{x^2-y^2}$ orbital empty. Thus the configuration of  $d^4$  ion in high spin octahedral complexes is  $(t_{2g})^3 (d_{z^2})^1 (d_{x^2-y^2})^0$  and not  $(t_{2g})^3 (d_{z^2})^0 (d_{x^2-y^2})^1$ . The repulsion between the single

electron present in  $d_{2}$  orbital and the two ligands along  $\pm z$ and -z axes (trans or axial ligands) results in the elongation of the two axial ligands. Thus the octahedral complex assumes elongated distorted octahedral structure in which two trans metal-ligand bonds are long and four metal-ligand bonds in xy square plane are short. In the formation of elongated distorted octahedral structure both  $t_{2g}$  and  $e_{g}$  sets present in octahedral complex split. The splitting of  $t_{2\sigma}^{s}$  and  $e_{s}$  sets in various d-orbitals takes place in the way as shown at (c) of Fig. 7.43. This configuration show that  $d_{2}$  orbital has lower energy than  $d_{x^2-v^2}$  orbital and hence has one electron. The energy difference between  $d_{xy}$  and  $d_{yz}$ ,  $d_{zx}$  pair is very small and hence each of these orbitals also has one electron only. Example of elongated distorted octahedral complexes containing  $d^4$  ion are  $CaF_2$  and  $MnF_3$  crystals and  $[Mn(H_2O)_6]^{3+}$  and  $[Mg(C_2O_4)_3]^{3-}$  ion.  $CrF_2$  crystal has distorted rutile (TiO2) structure in which Cr2+ ion is octahedrally surrounded by six F<sup>-</sup> ions (ligands). The length of four Cr<sup>+2</sup> — F bonds in xy plane is 2.0Å each and that of the two  $Cr^{2+}$  — F bonds along z-axis is 2.43Å. Thus the crystal of CrF<sub>2</sub> has elongated distorted octahedral structure. Fig. 7.43 shows that the distribution of  $d^4$  electrons in the splitted *d*-orbitals is as  $d_{yz}^1 d_{zx}^1 d_{xy}^1 d_{z^2}^1 d_{x^2-y^2}^0$ .

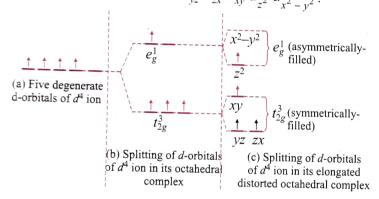


Fig. 7.43 Distribution of  $d^4$  electrons in octahedral and tetragonally elongated distorted octahedral complexes of  $d^4$  ion.

- **(b)**  $d^4$ (LS) ion: E.C. of  $d^4$  ion in LS state is  $t_{2g}^4 e_g^0$  which contains asymmetrically filled  $t_{2g}$  orbitals and empty  $e_g$  orbitals. LS octahedral complexes of  $d^4$  ion, therefore, show slight distortion.
- **6.** (a)  $d^5$ (HS) ion (e.g.  $Mn^{2+}$ ,  $Fe^{2+}$  etc.): E.C. of  $d^5$  ion is HS state is  $t_{2g}^3$   $e_g^2$  (n=5). This configuration shows that  $t_{2g}$  and  $e_g$  orbitals both are symmetrically filled. Hence HS octahedral complexes of  $d^5$  ion do not undergo any distortion. Examples of such complexes are  $[MnF_6]^{4-}$ ,  $[FeF_6]^{3-}$  etc.
  - **(b)**  $d^5$ (**LS)** ion: E.C. of  $d^5$  ion in LS state is  $t_{2g}^5 e_g^0$  (n = 1). This configuration has asymmetrically filled  $t_{2g}$  orbitals and empty  $e_g$  orbitals. Hence LS octahedral complexes of  $d^5$  ion undergo slight distortion.
- 7. (a)  $d^6$ (HS) ion (e.g.  $Co^{2+}$  ion): E.C. of  $d^6$  ion in HS state is  $t_{2g}^4 e_g^2$  (n=4). This configuration has asymmetrically filled  $t_{2g}$  orbitals and symmetrically filled  $e_g$  orbitals. HS

octahedral complexes of  $d^6$  ion, therefore, undergo slight distortion. Example of such complex is  $[CoF_6]^{3-}$ . (b)  $d^6$ (LS) ion (e.g.  $Co^{3+}$  ion): E.C. of  $d^6$  ion in LS states is  $t_{2g}^4 e_g^0$  (n=0). This configuration has symmetrically filled  $t_{2g}$  orbitals and empty  $e_g$  orbitals. Hence LS octahedral complexes of  $d^6$  ion undergo no distortion. Example of such octahedral complex is  $[Co(NH_1)_1]^{3+}$ 

- **8.** (a)  $d^7$  (HS) ion: E.C. of  $d^7$  ion in HS state is  $t_{2g}^5 e_g^2$  (n=3). This configuration has asymmetrically filled  $t_{2g}$  orbitals and symmetrically filled  $e_g$  orbitals. HS octahedral complexes of  $d^7$  ion, therefore, show slight distortion.
  - (b)  $d^7$  (LS) ion (e.g.  $Co^{2+}$ ): E.C. of  $d^7$  ion is LS octahedral complexes of this ion is  $t_{2g}^6 e_g^1$  (n=1). This configuration has symmetrically filled  $t_{2g}$  orbitals and asymmetrically filled  $e_g$  orbitals,  $e_g^1$  electrons is present in  $d_{x^2}$  orbital and  $d_{x^2-y^2}$  orbital is vacant. Thus  $t_{2g}^6 e_g^1 = t_{2g}^6 d_{z^2}^1 d_{z^2-y^2}^1 d_{x^2-y^2}^1$ . Due to the presence of asymmetrically-filled  $e_g$  orbitals in  $t_{2g}^6 e_g^1$  configuration, LS octahedral complexes of  $d^7$  ion undergo large distortion. [Co(diars)<sub>3</sub>]<sup>2+</sup> is an example of octahedral complex which undergoes large distortion.
- 9. (a)  $d^8$  ion (HS) (e.g. Ni<sup>2+</sup>): E.C. of  $d^8$  ion in HS state is  $t_{2g}^6 e_g^2 = t_{2g}^6 d_{z^2}^1 d_{x^2-y^2}^1$  (n=2). In this configuration  $t_{2g}$  and  $e_g$  orbitals both are symmetrically filled. Hence HS octahedral complexes of  $d^8$  ion do not show any distortion. Examples of such complexes are  $[NiF_6]^4$ ,  $[Ni(H_2O)_6]^2$ ,  $[Ni(NH_3)_6]^{2+}$  etc. Energy level diagram showing the filling of 3d orbitals with  $d^8$  electrons is given in Fig. 7.44.

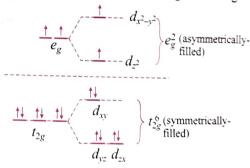


Fig. 7.44 Energy level diagram showing the filling of 3d orbitals with eight electrons of d<sup>8</sup> configuration in HS sate

(b)  $d^8$  (LS) ion (e.g., Ni<sup>2+</sup>, Pd<sup>2+</sup>, Pt<sup>2+</sup> etc.): E.C. of  $d^8$  ion in LS state is  $t_{2g}^6 e_g^2 = t_{2g}^6 d_{z^2}^2 d_{x^2-y^2}^0$  (n=0). In this configuration,  $t_{2g}$  orbitals are symmetrically filled. Although  $e_g$  orbitals are half filled, these orbitals are said to be asymmetrically filled, since both the  $e_g$  electrons are present in  $d_{z^2}$  orbital. Hence LS octahedral complexes of  $d^8$  ion show large distortion giving elongated distorted octahedral geometry. Examples of such complexes are [Mg(diars)<sub>2</sub>I<sub>2</sub>]<sup>0</sup> where M = Ni<sup>2+</sup>, Pd<sup>2+</sup>, Pt<sup>2+</sup>.

The splitting of  $t_{2g}$  (lower energy) and  $e_g$  (higher energy) orbitals in elongated distorted octahedral complexes takes place as shown in Fig. 7.45. This figure shows that the distribution of  $d^8$  electrons in the splitted d-orbitals is as  $d_{yz}^2 d_{zx}^2 d_{xy}^2 d_{z}^2 d_{yz}^2 = v^2$ .

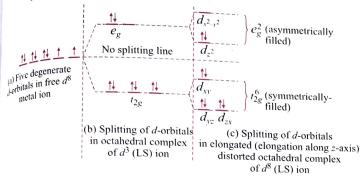


Fig. 7.45 Splitting of d-orbitals in tetragonally elongated octahedral complexes of d<sup>8</sup> in LS state

10.  $d^9$  ion (e.g.  $Cu^{2+}$  ion): E.C. of  $d^9$  ion ( $Cu^{2+}$  ion) is  $t_{2g}^6 e_g^2$  (n=1). In this configuration  $t_{2g}$  orbitals are symmetrically filled but both  $e_g$  orbitals are asymmetrically filled. It is due to the presence of a symmetrically filled  $e_g$  orbitals that octahedral complexes of  $Cu^{2+}$  ion undergo large distortion

and assume either elongated distorted octahedral geometry or compressed distorted octahedral geometry. If  $t_{2g}^6 e_g^3$  configuration is  $t_{2g}^5 d_{z^2}^2 d_{x^2-y^2}^1$ , octahedral geometry assumes elongated distorted octahedral geometry. On the other hand, if  $t_{2g}^6 e_g^3$  configuration is  $t_{2g}^6 d_{z^2}^1 d_{x^2-y^2}^2$ , the octahedral geometry assumes compressed distorted octahedral geometry.

The splitting of  $t_{2g}$  and  $e_g$  orbitals in elongated distorted octahedral and compressed distorted octahedral geometry has been discussed on the subsequent pages of this chapter.

11.  $d^{10}$  ion (e.g.  $Zn^{2+}$ ). E.C. of  $d^{10}$  ion is  $t_{2g}^6 e_g^4$ . This configuration has  $t_{2g}$  and  $e_g$  orbitals both symmetrically filled. Hence octahedral complexes of  $d^{10}$  ion do not show distortion. Examples of such complexes are  $[Zn(NH_3)_6]^{2+}$ ,  $[Zn(H_2O)_6]^{2+}$  etc.

Whatever has been said above has been summarized in Table 7.21. The information given in this table can be used to find out the conditions under which the octahedral complex of a given  $d^x$  ion (x = 0 to 10) undergoes no distortion, slight distortion or large distortion.

Table 7.21 Summary of distortion taking place in octahedral complexes of d<sup>x</sup> ions (x = 0 to 10), sym. = symmetrically filled, asym. = asymmetrically filled.

d <sup>x</sup> ion (x = 0 to 10)	$t^a_{2g}e^b_g$ configuration	Nature of $t_{2g}$ and $oldsymbol{e}_g$ orbitals		Distortion	
		$t_{2g}$ $e_g$			
$d^0$	$t_{2g}^0e_g^0$	Empty	Empty	No distortion	
$d^1$	$t_{2g}^{1} e_{g}^{0} = d_{xy}^{1} d_{yz}^{0} d_{xz}^{0} e_{g}^{0}$	Asym	Empty	Strong distortion (Compressed distortion)	
	$t_{2g}^{1} e_{g}^{0} = d_{xy}^{0} d_{yz}^{1} d_{xz}^{0} e_{g}^{0} \text{ or } d_{xy}^{0} d_{yz}^{0} d_{xz}^{1} e_{g}^{0}$	Asym	Empty	Large distortion (Elongated distortion)	
$d^2$	$t_{2g}^2 e_g^0$	Asym	Empty	Slight distortion	
$d^3$	$t_{2g}^3 e_g^0$	Asym	Empty	No distortion	
d <sup>4</sup> (HS)	$t_{2g}^{3} e_{g}^{1} = t_{2g}^{3} d_{z^{2}}^{1} d_{x^{2} - y^{2}}^{0}$	Asym	Asym	Strong distortion (Elongated distortion)	
<i>d</i> <sup>4</sup> (LS)	$t_{2g}^4 e_g^0$	Asym	Asym	Slight distortion	
<i>d</i> <sup>5</sup> (HS)	$t_{2g}^3 e_g^2$	Sym	Sym	No distortion	
$d^{5}$ (LS)	$t_{2g}^5 e_g^0$	Asym	Empty	Slight distortion	
<i>d</i> <sup>6</sup> (HS)	$t_{2g}^4 e_g^2$	Asym	Sym	Slight distortion	
<i>d</i> <sup>6</sup> (LS)		Sym	Empty	No distortion	
	$t_{2g}^6 e_g^0$	Asym	y Sym	Slight distortion	
d <sup>7</sup> (HS)	$t_{2g}^5 e_g^2$				

$d^7$ (LS)	$t_{2g}^{6} e_{g}^{1} = t_{2g}^{6} d_{z^{2}}^{1} d_{y^{2}-y^{2}}^{0}$	Sym	Asym	Large distortion
d <sup>8</sup> (HS)	$t_{2g}^{6} e_{g}^{2}$	Sym	Sym	No distortion
d <sup>8</sup> (LS)	$t_{2g}^{6} e_{g}^{2} = t_{2g}^{6} d_{z^{2}}^{2} d_{y^{2} - y^{2}}^{0}$	Sym	Asym	Large distortion (Elongated distortion)
d <sup>9</sup>	$t_{2g}^{6} e_{g}^{3} = t_{2g}^{6} d_{z^{2}}^{2} d_{x^{2} - y^{2}}^{1}$	Sym	Asym	Large distortion (elongated distortion)
d <sup>9</sup>	$t_{2g}^6 e_g^3 = t_{2g}^6 d_{z^2}^1 d_{x^2 - y^2}^2$	Sym	Asym	Large distortion (elongated distortion)
$d^{10}$	$t_{2g}^2 e_g^4$	Sym	Sym	No distortion

### 7.12.3.1 Conditions for No Distortion

Octahedral complexes of  $d^x$  ions whose both the sets of d-orbitals viz  $t_{2g}$  and  $e_g$  are symmetrically filled  $(t_{2g}^0, t_{2g}^3, t_{2g}^6)$  and  $e_g^0, e_g^2, e_g^4)$  undergo no distortion, i.e., such complexes are perfectly octahedral in shape. Perfectly octahedral shape is because of the fact that the electrons present in symmetrically filled  $t_{2g}$  and  $e_g$  sets repell all the six ligands to the same extent. This discussion shows that since the ions viz  $d^0(t_{2g}^0e_g^0, n=0)$ ,  $d^3(t_{2g}^3e_g^0, n=3)$ ,  $d^5(t_{2g}^3e_g^2-\text{HS} \text{ with } n=5)$ ,  $d^6(t_{2g}^6e_g^0-\text{LS} \text{ with } n=0)$ , and  $d^8(t_{2g}^6e_g^2-\text{HS} \text{ with } n=2)$   $d^{10}(t_{2g}^5e_g^4 \text{ with } n=0)$  have  $t_{2g}$  and  $e_g$  sets symmetrically filled,

### 7.12.3.2 Conditions for Slight (Negligible) Distortion

these complexes are perfectly octahedral.

octahedral complexes of these ions do not undergo distortion, i.e.,

Octahedral complexes of  $d^x$  ions whose  $t_{2g}$  set of orbitals is asymmetrically-filled  $(t_{2g}^1, t_{2g}^2, t_{2g}^4, t_{2g}^5)$  and  $e_g$  sets is symmetrically-filled  $(e_g^0, e_g^2)$  undergo slight distortion. Small distortion is because of the fact that since the lobes the three asymmetrically-filled orbitals of  $t_{2g}$  set do not lie directly in the path of the ligands, the electrons present in  $t_{2g}$  set of orbitals cause small distortion in octahedral complexes. Thus the octahedral complexes  $d^2(t_{2g}^2 e_g^2, n = 0)$ ,  $d^4(t_{2g}^4 e_g^0 - \text{LS with } n = 2)$ ,  $d^5(t_{2g}^5 e_g^0 - \text{LS with } n = 1)$ ,  $d^5(t_{2g}^4 e_g^2 - \text{HS with } n = 4)$ , and  $d^7(t_{2g}^5 e_g^2 - \text{HS with } n = 3)$  ions undergo small distortion.

## 7.12.3.3 Conditions for Large Distortion

Octahedral complexes of  $d^x$  ions whose  $t_{2g}$  set is symmetrically-filled  $(t_{2g}^0, t_{2g}^3 \text{ and } t_{2g}^6)$  and  $e_g$  set is asymmetrically-filled  $[e_g^1(d_{z^2}^1 d_{x^2-y^2}^0), e_g^3(d_{z^2}^2 d_{x^2-y^2}^1)] = e_g^3(d_{x^2-y^2}^0 d_{z^2}^1) [e_g^2 \text{ set} (d_{z^2}^2 d_{x^2-y^2}^0)]$  is also regarded as asymmetrically-filled set in LS

octahedral complexes of  $d^8$  ion  $(d^8 = t_{2g}^6 e_g^2 = t_{2g}^6 d_{z^2}^2 d_{x^2 - y^2}^0)$ ] undergo strong distortion and assume either tetragonally elongated distorted octahedral geometry or compressed distorted octahedral geometry.

Thus the octahedral complexes of the following  $d^r$  ions undergo strong (large) distortion.

$$d^{1}(t_{2g}^{1} e_{g}^{0}), d^{4}(\mathrm{HS})(t_{2g}^{3} d_{z^{2}}^{1} d_{x^{2}-y^{2}}^{0} - \mathrm{elongated\ distortion}),$$

$$d^{7}(\mathrm{LS})(t_{2g}^{6} e_{g}^{1} = t_{2g}^{6} d_{z^{2}}^{1} d_{x^{2}-y^{2}}^{0}),$$

$$d^{8}(\mathrm{LS})(t_{2g}^{6} e_{g}^{2} = t_{2g}^{6} d_{z^{2}}^{2} d_{x^{2}-y^{2}}^{0} - \mathrm{elongated\ distortion}),$$

$$d^{9}(t_{2g}^{6} e_{g}^{3} = t_{2g}^{6} d_{z^{2}}^{2} d_{x^{2}-y^{2}}^{1} - \mathrm{elongated\ distortion}),$$

$$d^{9}(t_{2g}^{6} e_{g}^{3} = t_{2g}^{6} d_{z^{2}}^{1} d_{x^{2}-y^{2}}^{2} - \mathrm{compressed\ distortion}).$$

Cause of large (strong) distortion: Since the lobes of both orbitals of  $e_g$  set  $(d_{z^2}$  and  $d_{z^2-y^2}$  orbitals) lie directly in the path of the six ligands (six ligands of an octahedral complex lie on the three axes), the electrons present in this set, if arranged asymmetrically) i.e., if  $e_g$  set contains 1 or 3 electrons), repell some ligands to greater extent and repel other ligands to lesser extent. This ligand repulsion causes large distortion in octahedral shape of 6-coordinated complexes.

# 7.12.3.4 Splitting of $t_{2g}$ and $e_g$ Orbitals in Elongated Distorted Octahedral Complexes of ${\rm Cu}^{2^+}$ lon

The splitting of  $t_{2g}$  and eg sets of orbitals into various *d*-orbitals has been shown in Fig. 7.46

In order to explain the splitting pattern shown in Fig. 7.46, we start with the splitting of d-orbitals in  $t_{2g}$  and  $e_g$  sets in octahedral complexes. We know that in the splitting of d-orbitals in octahedral complexes, the energy of  $t_{2g}$  set (i.e.  $d_{xy}$ ,  $d_{yz}$  and  $d_{zx}$  orbitals) is decreased and that of  $e_g$  set (i.e.,  $d_{z2}$  and  $d_{x^2-y^2}$  orbitals) is increased. Now in elongated distorted octahedral complexes, since metal-ligand bond distance along z-axis is longer, d-orbitals having z component (i.e.,  $d_{yz}$ ,  $d_{zx}$  and  $d_{z^2}$  orbitals) experience less repulsion from the ligands than they do in octahedral complex

while the *d*-orbitals in xy plane (i.e.,  $d_{xy}$  and  $d_{x^2-y^2}$  orbitals) experience more repulsion than they do in octahedral complex. Consequently the energy of  $d_{yz}$ ,  $d_{zx}$  and  $d_{z^2}$  orbitals decreases while that  $d_{xy}$  and  $d_{x^2-y^2}$  orbitals increases. Note that  $d_{yz}$  and  $d_{zx}$  and  $d_{zx}$  and  $d_{zy}$  and  $d_{zx}$  and  $d_{zy}$  and  $d_{zx}$  and  $d_{zy}$  are in octahedral complex. Above discussion shows that the order of energy of the splitted-orbitals in tetragonally elongated octahedral complex becomes as:  $(d_{yz} = d_{zx}) < d_{xy} < d_{z^2} < d_{x^2-y^2}$  (Also see Fig. 7.46)

The relative order of energy of various orbitals shown above indicates that in the elongated distorted octahedral complexes the distribution of  $3d^9$  electrons  $(t_{2g}^6 e_g^3)$  of  $Cu^{2+}$  ion is as shown in Fig. 7.46. This figure shows that the arrangement of  $d^9$  electrons in various d-orbitals can be written as:

$$\underbrace{\frac{d_{yz}^2, d_{zx}^2, d_{xy}^2}{f_{2g}^6}}_{f_{2g}^6} \underbrace{\frac{d_{z^2}^2, d_{x^2-y^2}^1}{e_{\sigma}^3}}_{\frac{e_{\sigma}^3}}$$

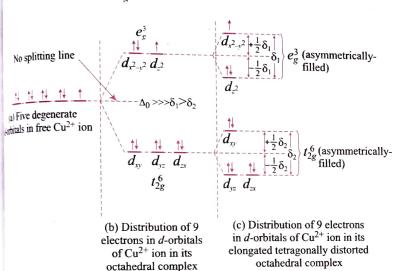


Fig. 7.46 Distribution of 9 electrons of  $Cu^{2+}$  ion  $(Cu^{2+} = 3d^9)$  in the splitted d-orbitals in its tetragonally elongated distorted octahedral complexes.

Thus the configuration,  $t_{2g}^6 e_g^3$  can be written as:

$$t_{2g}^6 e_g^3 = t_{2g}^6 d_{z^2}^2 d_{x^2 - y^2}^1$$

This configuration shows that tetragonally elongated octahedral complexes have two electrons in  $d_{z^2}$  orbital and one electron in  $d_{x^2-y^2}$  orbital, since  $d_{z^2}$  ortifial has lower energy than  $d_{x^2-y^2}$  orbital.

<sup>1</sup>12.3.5 Elongated Distortion in Octahedral Geometry of [Cu(NH<sub>3</sub>)<sub>4</sub>(H<sub>2</sub>O)<sub>2</sub>]<sup>2+</sup> and [Cu(H<sub>2</sub>O)<sub>6</sub>]<sup>2+</sup> Complexes

Tetrammine copper (II) complex,  $[Cu(NH_3)_4]^{2^+}$  is actually  $[Cu(NH_3)_4(H_2O)_2]^{2^+}$  in which the two axial  $H_2O$  ligands are at larger distances (along the z-axis) from the central  $Cu^{2^+}$  in the four equational  $NH_3$  ligands are of shorter distances (along x- and y-axes). Thus this complex has two long (axial) and four short (equational) bonds. Consequently the complex,  $[Cu(NH_3)_4(H_2O)_2]^+$  has tetragonally elongated distorted octahedral geometry

The distribution of  $d^9$  electrons of  $Cu^{2+}$  ion in five d-orbitals is as:

$$\frac{1}{yz} \frac{1}{zx} \begin{vmatrix} \frac{1}{xy} & \frac{1}{z^2} & \frac{1}{x^2 - y^2} \\ & & & & \\ & & \\ & & & \\ & & & \\ & & \\ & & & \\ & & \\ & & & \\ & & \\ & & \\ & & & \\ & & \\ & & & \\ & & \\ & & & \\ & & \\ & & & \\ & & & \\ & &$$

 $[\mathrm{Cu}(\mathrm{H_2O})_6]^{2^+}$  ion also has tetragonally elongated distorted octahedral geometry. The tetragonally elongated geometry (distorted octahedral geometry) of  $[\mathrm{Cu}(\mathrm{NH_3})_4(\mathrm{H_2O})_2]^{2^+}$  and  $[\mathrm{Cu}(\mathrm{H_2O})_6]^{2^+}$  ions is due to the asymmetric arrangement of three electrons in  $e_g$  orbitals. This arrangement contains two electrons in  $d_{z^2}$  orbital and one electron in  $d_{x^2-y^2}$  orbitals, since  $d_{z^2}$  orbital has lower energy than  $d_{x^2-y^2}$  orbital. The effect of the asymmetric arrangement of three electrons in  $e_g$  orbitals on the octahedral geometry of the complex ions is called Jahn-Teller effect.

# 7.13 TRANS EFFECT

Trans effect is the labialization (making more reactive) of ligands that are trans to certain other ligands, which can thus be regarded as trans, directing ligands. It is attributed to electronic effects and it is most notable in square planar complexes, although it can also be observed for octahedral complexes. The cis effect is most often observed in octahedral transition metal complexes.

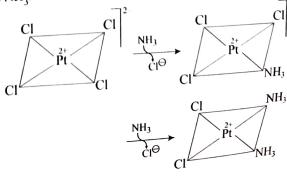
In addition to this kinetic trans effect, trans ligands also have an influence on the ground state of the molecule, the most notable ones being bond length and stability the term trans influence is sometimes used to distinguish it from kinetic effect however more specific terms such as structural trans effect or thermodynamic trans effect is also used.

The intensity of the trans effect (as measured by the increases in rate of substitution of trans ligand) follow this sequence.

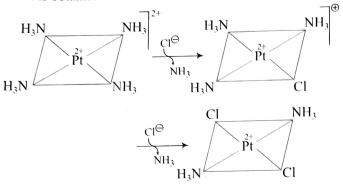
$$\begin{split} &C_{2}H_{4},CH^{\odot},CO,\!NO,H^{\odot}>CH_{3}^{\odot},SR_{2},AsR_{3},\\ &PR_{3}>SO_{3}^{-2}>C_{6}H_{5}^{\odot},SC(NH_{2})_{2},NO_{2}^{\odot},SCN^{\odot}\\ &>I^{\odot}>Br^{\odot}>Cl^{\odot}>py>NH_{3}>OH^{\odot},H_{2}O,F^{\odot} \end{split}$$

- (i) (CN<sup>o</sup>, CO and NO are powerful trans directions while OH and H<sub>2</sub>O are very poor.)
- (ii) M—X bond is more labile than M—N bond.

**Example:** The classical example of the trans effect is the synthesis of **cisplatine** and its trans isomer. Starting from  $[PtCl_4]^{2-}$ , the first NH<sub>3</sub> ligand is added to any of the four equivalent position at random. However since  $Cl^{\odot}$  has a greater trans effect than NH<sub>3</sub>, the second NH<sub>3</sub> is added trans to a  $Cl^{\odot}$  and therefore cis to the first NH<sub>3</sub>.



If, on the other hand, one starts from  $[Pt(NH_3)_4]^{2+}$ , the trans product is obtained instead:



**Explanation:** The trans effect in square planar complexes can be explained in terms of an addition/elimination mechanism that goes through a trigonal bypyramidal intermediate ligands with a high trans effect are in general those with high  $\pi$ -acidity (as in case of phosphine, PH<sub>3</sub>) or low-ligand lone pair-  $d\pi$  repulsions (as in case of hydride, H<sup>2</sup>), which prefer the more  $\pi$ -basic equatorial sites in the intermediate. The second equatorial position is occupied by the incoming ligand, due to the principle of microscopic reversibility, the departing ligand must also leave from an equatorial position. The third and final equatorial site is occupied by the trans ligand, so the net result is that the kinetically favoured product is the one in which the ligand trans to the one with the largest trans effect is eliminated.

**Structural trans effect:** The structural trans effect can be measured experimentally using x-ray crystallography, and is observed as a stretching of the bonds between the ligand and the ligand trans to a trans-influencing ligand.

Stretching by as much as 0.2Å occurs with strong transinfluencing ligands such as hydride (H<sup>o</sup>) ion. A cis influence can also be observed, but is smaller than the trans influence. The relative importance of cis and trans influences depends on the formal electronic configuration of metal center, and explanations have been proposed based on the involvement of the atomic orbitals.

**Factors:** The trans effect is used to distinguish between the cis and the trans isomers of the type  $[Pt A_2X_2]$  where A = amine and X = halide.

- (i) Thiourea (tu) replaces the halides only in the trans isomer but all the four ligands are replaced in the cis-isomer.
- (ii) Trans effect is important with the large polarizable metal ions, the order of metals is:  $Pt^{+2} > Pd^{+2} > Ni^{+2}$ .
- (iii) The trans directors are either polarizable (I<sup>⊙</sup>) or multiple bonded (CO, CN<sup>⊙</sup> etc.).
- (iv) The two  $\pi$ -ligands, for the d-orbitals of the metal ion, will tend to labilize each other when present trans to each other, but in the cis-position they will not complete.
- (v) The stronger  $\pi$ -bonding ligand will dominate and weaken the other bond.
- (vi) In  $[Pt\ Cl_3(C_2H_4)]^{\odot}$ , the Pt—Cl bond trans to  $(C_2H_4)$  (ethylene) is larger than the cis-bond.
- (vii) Pt—Cl (trans) stretching frequency is lower than the P—Cl (cis) frequencies showing weaker Pt—Cl bonds trans to ethylene group.

### Limitation

- (i) Ammonia which cannot form  $\pi$ -bonds should not be destabilized by the  $\pi$ -bonding ligands.
- (ii)  $\pi$ -bonding alkenes show trans effect for halogens but not for the nitrogen ligands.
- (iii) Many ligands like hydride (H $^{\circ}$ ) or methyl are good  $_{trans}$  directors but cannot form  $\pi\text{-bond}$ .

# ILLUSTRATION 7.54

The correct increasing order of trans-effect of the following species is:

**a.** 
$$CN^{\odot} > Br^{\odot} > C_6H_5^{\odot} > NH_3$$

**b.** 
$$NH_3 > CN^{\odot} > Br^{\odot} > C_6H_5^{\odot}$$

**c.** 
$$CN^{\odot} > C_6H_5^{\odot} > Br^{\odot} > NH_3$$

**d.** 
$$Br^{\odot} > CN^{\odot} > NH_3 > C_6H_5$$

**Sol.** c. The intensity of trans effect-depends on increase in rate of substitution of the trans ligands  $CN^{\odot} > CH_3^{\odot} > C_6H_5^{\odot} > Br^{\odot} > Cl^{\odot} > NH_3 > F^{\odot}$ .

# ILLUSTRATION 7.55

Jahn-Teller effect is not observed in high spin complexes of

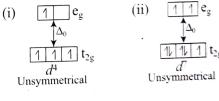
$$\mathbf{a}. d^9$$

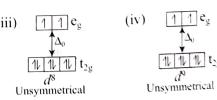
b. a

d. d4

**Sol. c.** Jahn Teller effect: This is geometric distortion which occurs in unsymmetrical octahedral complexes.

For example: High spin complexes of (high spin)





Jahn Teller effect is not observed in  $d^8$  configuration.

# ILLUSTRATION 7.56

Explain the following giving reasons:

- **a.**  $[\text{NiCl}_4]^2$  is tetrahedral and paramagnetic, whereas  $[\text{Ni(CN)}_4]^2$  is square planar and dimagnetic.
- **b.**  $[Fe(H_2O)_6]^{3+}$  ion is more paramagnetic than  $[Fe(CN)_6]^{3-}$  ion.
- c.  $Ni(CO)_4$  is tetrahedral while  $[Ni(CN)_4]^2$  ion is square planar.
- **d.**  $[Co(F_6)]^{3-}$  is a high spin complex whereas  $[Co(CN)_6]^{3-}$  ion is a low spin complex.

	Electronic configuration of $Fe^{3+}$ in $Fe(CN)_6]^{3-}$ ion
	i.e. there is only one unpaired electron, $n = 1$ . Since in $[Fe(H_2O)_6]^{3^+}$ ion, number of unpaired electrons are more than $[Fe(CN)_6]^{3^-}$ ion, $[Fe(H_2O)_6]^{3^+}$ is more paramagnetic than $[Fe(CN)_6]^{3^-}$ ion.
с.	In Ni(CO) <sub>4</sub> , oxidation state of Ni is zero.
	Electronic $3d$ $4s$ $4p$ configuration of Ni atom $(3d^8 4s^2)$
	Since CO is strong field ligands, hence pairing of electrons takes place.
	Ni atom in [Ni(CO) <sub>4</sub> ] $ \begin{array}{c c} 3d & 4s & 4p \\ \hline 1 & 1 & 1 & 1 & 1 \\ \hline & & & & \\ \hline & & & & \\ \hline & & & & \\ \hline & & & &$
	Because of $sp^3$ hybridisation, $[Ni(CO)_4]$ is tetrahedral.
	In $[Ni(CN)_4]^{2-}$ , oxidation state of Ni is +2
	Ni atom $ \begin{array}{c ccccccccccccccccccccccccccccccccccc$
	Ni <sup>2+</sup> atom
	Since $CN^{\Theta}$ is strong field which results in pairing up of electron present in $3d_{x^2-y^2}$ and $3d_{z^2}$ and $3d_{x^2-y^2}$ becomes available for $dsp^2$ hybridisation.
	$ \begin{array}{cccccccccccccccccccccccccccccccccccc$
d	1. $[CoF_6]^{3-}$ is a high spin complex whereas $[Co(CN)_6]^{3-}$ is a low spin complex. This can be explained as: $3d \qquad 4s \qquad 4p \qquad 4d$
	Co atom $(3d^7 4s^2)$
	Co <sup>3+</sup> ion $(3d^7 4s^0)$ [1111111] $(n = 4)$

available for  $dsp^2$  hybridisation which gives square planar geometry with n = 0. Thus  $[Ni(CN)_4]^{2-}$  is diamagnetic. b. Oxidation state of Fe in  $[Fe(H_2O)_6]^{3+}$ ion is +3. Electronic configuration of Fe  $(3d^6 4s^2)$ Electronic configuration of Fe<sup>3+</sup> ion  $(3d^5 4s^0)$ Since H<sub>2</sub>O is weak field ligand, no pairing of electrons takes place and Electronic configuration of Fe<sup>3+</sup> in  $[Fe(H_2O)_6]^{3+}$  ion 1.e. there are 5 unpaired electrons, n = 5. Whereas in  $[Fe(CN)_6]^{3-}$ , oxidation state of Fe is +3.

In the complex,  $[NiCl_4]^{2-}$  and  $[Ni(CN)_4]^{2-}$  oxidation state

Since Cl<sup>©</sup> ion is weak field ligand, electronic configuration

Since  $Ni^{2+}$  in  $[NiCl_4]^{2-}$  ion is  $sp^3$  hybridised and have two unpaired electrons it is tetrahedral and paramagnetic. Since CN ion is strong field ligand, electronic configuration

i.e., one electron from  $3d_{\chi^2-y^2}$  orbital gets paired with that in  $3d_{2}$  orbital. Thus one *d*-orbital  $(3d_{x^2-y^2})$  orbital) becomes

Electronic  $3d^8 4s^2 \boxed{11111}$ 

of Ni<sup>2+</sup> in [NiCl<sub>4</sub>]<sup>2-</sup> remains the same,

configuration of Ni atom

of Ni<sup>2+</sup> ion

Ni<sup>2+</sup> ion  $in [NiCl_4]^{2-}$ 

Electronic  $3d^8 4s^0$ 

of  $Ni^{2+}$  in  $[Ni(CN)_4]^{2-}$  is

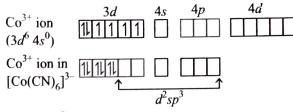
Since F<sup>©</sup> ion is weak field ligand, no pairing up of electrons present in 3d orbital takes place. Since there are four unpaired electrons, [CoF<sub>6</sub>]<sup>3-</sup> is paramagnetic complex. Since outer d orbitals (i.e. 4d) are involved, it is also known as high spin or outer orbital complex.

3d Electronic configuration of Fe<sup>3+</sup> ion  $(3d^5 4s^0)$ 

Note: Oxalate generally behaves as a weak field ligand but with Co, it behaves as a strong field ligand like NH3

Since  $CN^{\Theta}$  ion is strong field ligand, pairing up of electrons in 3d orbitals takes place i.e.

In  $[Co(CN)_6]^{3-}$ , oxidation state of Co is +3.



Since  $CN^{\Theta}$  is a strong field ligands, pairing of 3d electrons takes place, n = 0. Since inner d orbitals (3d) are involved in hybridisation  $(d^2sp^3)$ , it is also known as low spin or inner orbital complex.

In  $[CoF_6]^{3-}$ , n = 4 whereas in  $[Co(CN)_6]^{3-}$ , n = 0 hence  $[CoF_6]^{3-}$  is a high spin complex whereas  $[Co(CN)_6]^{3-}$  is a low spin complex.

# 7.14 STABILITY OF COORDINATION COMPOUNDS IN SOLUTIONS

For the reaction,

The stability of the coordination compound  $[ML_n]$  is measured in terms of the overall stability constant (equilibrium constant) given by the expression.

$$\beta_{n} = [ML_{n}] / [M(H_{2}O)_{n}] [L]^{n}$$

The above reaction, takes place in steps.

A coordination compound is formed in solution by the stepwise addition of ligands to a metal ion. Thus formation of the complex.  $ML_n$  may be supposed to take place by the consecutive n steps.

$$[\mathbf{M}(\mathbf{H}_2\mathbf{O})_n] + \mathbf{L} \Longrightarrow [\mathbf{M}\mathbf{L}(\mathbf{H}_2\mathbf{O})_{n-1}] + \mathbf{H}_2\mathbf{O}$$
 
$$\mathbf{K}_1 = \frac{[\mathbf{M}\mathbf{L}(\mathbf{H}_2\mathbf{O})_{n-1}]}{[\mathbf{M}(\mathbf{H}_2\mathbf{O})_n][\mathbf{L}]}$$

$$[\mathsf{ML}(\mathsf{H}_2\mathsf{O})_{n-1}] + \mathsf{L} \Longrightarrow [\mathsf{ML}(\mathsf{H}_2\mathsf{O})_{n-2}] + \mathsf{H}_2\mathsf{O}$$

$$K_2 = \frac{[ML(H_2O)_{n-2}]}{[M(H_2O)_{n-1}][L]}$$

$$[ML_{n-1}(H_2O)] + L \Longrightarrow [ML_n] + H_2O$$

$$K_n = \frac{[ML_n]}{[ML_{n-1}(H_2O)][L]}$$

$$[M(H_2O)_n] + nL \Longrightarrow [ML_n] + nH_2O$$

$$\beta_n = K_1 \times K_2 \times K_3 \cdots K_n = \frac{[ML_n]}{[M(H_2O)_n [L]^n}$$

By convention, the water, H<sub>2</sub>O displaced is ignored, as its concentration remains essentially constant.

 $K_1, K_2, \dots K_n$  are called stepwise stability constant. In general, the values of successive stability constants decrease regularly from  $K_1$  to  $K_n$ .  $\beta_n$  is called the overall stability constant (and  $1/\beta_n$  is called as instability constant). The higher the overall stability constant value of the complex, the more stable it is. Alternatively, values called instability constant explain the dissociation of the complex into metal ion and ligands in the solution.

 $\beta_n$ , the overall stability constant is related to thermodynamic stability when the system has reached equilibrium. Stability constants of few complexes in solution are given in the following table.

System	Stability constant K
$Cu^{2+} + NH_3 \Longrightarrow [Cu(NH_3)_4]^{2+}$	4.5 × 10 <sup>11</sup>
$Cu^{2+} + 4CN^{\Theta} \Longrightarrow [Cu(CN)_4]^{2-}$	$2.0 \times 10^{27}$
$Ag^{\oplus} + 4NH_3 \Longrightarrow [Ag(NH_3)_2]^{\oplus}$	$1.6 \times 10^{7}$
$\operatorname{Co}^{3+} + 6\operatorname{NH}_3 \Longrightarrow \left[\operatorname{Co}(\operatorname{NH}_3)_6\right]^{3+}$	$5.0 \times 10^{33}$
T 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1	m - A

From the above values it is seen that  $CN^{\Theta}$  is a stronger ligand than  $NH_3$ .

Important generalisations derived from the vast data on stability constants are as follows:

a. For a given metal and ligand the stability is generally greater, the greater the charge on the metal ion. Thus, stability of coordination entities of ions of charge 3+ is greater than the entities of 2 ions. Further, for the divalent ions of the first row transition elements, irrespective of the ligand involved, the stabilities vary in the **Irving-Williams Order**:

$$Mn^{II} \le Fe^{II} \le Co^{II} \le Ni^{II} \le Cu^{II} \le Zn^{II}$$

- b. The metal ions, 'class a' acceptors like metals of groups 1 and 2, the inner transition elements and the early members of the transition series (groups 3 to 6) form their most stable coordination entities with ligands containing N, O or F donor atoms.
- c. The metal ions, 'class b' acceptors like the transition elements—Rh, Pd, Ag, Ir, Au and Hg having relatively full d orbitals form their most sable complexes with ligands whose donor/atoms are the heavier members of the N, O and F groups.
- d. The stability also depends on the formation of chelate rings. If L is an unidentate ligand and L-L, a didentate ligand and if the donor atoms of L and L-L are the same element, then L-L will replace L. The stabilisation due to chelation is called the chelate effect. It is of great importance in biological systems and analytical chemistry. The chelate effect is maximum for the 5- and 6-membered rings. In general, rings provide greater stability to the complex.
- e. If a multidentate ligand happens to be cyclic and there are no unfavourable steric effects, a further increase in stability occurs. This is termed the macrocyclic effect.

# 7.15 COLOUR IN COORDINATION COMPOUNDS

Coordination compounds of transition metal have fascinating colours. The study of the colour of transition metal complexes can be divided into two categories:

# 4. Colour of the complex ions whose central metal atom contains partially filled d-orbitals.

when white light which is composed of many different colours falls on a coloured complex ion or complex compound of a transition metal, the ion or complex absorbs some portion of the white light and the remaining portion of the incident light is transimitted or reflected by the complex/ion. The colour of absorbed light and transmitted are different from each other. The colour of the transmitted light is called complimentary colour of the adsorbed light, oiven in Table 7.22. The complimentary colour is the colour generated from the wavelength left over.

7.22 Colour of absorbed and transmitted radiations

colour of the absorbed light/radiation	Range of the wavelength (Å) of the absorbed light	Colour of the transmitted light (complimentary colour of the absorbed light
Violet	4000 - 4500	Yellow green
Blue	4500 – 4800	Yellow
Green blue	4800 – 4900	Orange
Blue green	4900 - 5000	Red
Green	5000 - 5600	Violet (almost purple)
Yellow green	5600 - 5750	Violet
Yellow	5750 - 5900	Blue
Orange	5900 - 6250	Green blue
Red	6250 - 7500	Blue green

### For example:

- i. Hydrated  $\text{Cu}^{2^+}$  ion, i.e.  $[\text{Cu}(\text{H}_2\text{O})_4]\text{SO}_4\cdot\text{H}_2\text{O}$  or  $\text{CuSO}_4\cdot\text{5H}_2\text{O}$ absorbs yellow radiation and transmits blue radiation and hence looks blue to our eyes.
- ii. Hydrated Ti<sup>3+</sup> ion, [Ti(H<sub>2</sub>O)<sub>6</sub>]<sup>3+</sup> absorbs green radiation hence transmits the radiation of purple colour. Hydrated Ti<sup>3+</sup> ion, therefore looks violet (almost purple).
- iii. Anhydrous Co<sup>3+</sup> compounds absorb the radiation of red colour and therefore appear blue green. Whereas, hydrated  $\text{Co}^{2+}$  ion i.e.  $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$  ion absorbs blue green radiation and therefore appears red.

Colours of some common hexahydrated transition metal complex ions  $[M(H_2O)_6]^{n+}$  are given in Table 7.23.

Table 7.23 Colours of some common  $[M(H_2O)_6]^{n+}$  ions

lons	Electronic configuration	Colour of the ion violet
j <sup>3+</sup>	$3d^1\ (n=1)$	Violet (almost purple)
3+	$3d^2\ (n=2)$	Green
$^{2+}$ , $Cr^{3+}$	$3d^3\ (n=3)$	Violet

Cr <sup>2+</sup>	$3d^4\ (n=4)$	Blue
Mn <sup>3+</sup>	$3d^4\ (n=4)$	Violet
Mn <sup>2+</sup>	$3d^5\ (n=5)$	Pink
Fe <sup>3+</sup>	$3d^5 (n=5)$	Yellow
Fe <sup>2+</sup>	$3d^6 (n=4)$	Green
Co <sup>2+</sup>	$3d^7 (n=3)$	Pink (red)
Ni <sup>2+</sup>	$3d^8\ (n=2)$	Blue green
Cu <sup>2+</sup>	$3d^9 (n=1)$	Blue

Colours of transition metal ions in aqueous solution corresponds to their aqua complexes.

Following table gives the wavelength of light adsorbed and the coloured observed in some coordination entities.

Table 7.24 Relationship between the wavelength of light absorbed and the colour observed in some coordination entities

Coordination entities	Wavelength of light absorbed (nm)	Colour of light absorbed	Colour of coordination entity
[CoCl(NH3)5]2+	535	Yellow	Violet
$[Co(NH_3)_5(H_2O)]^{3+}$	500	Blue green	Red
$\left[\mathrm{Co(NH_3)_6}\right]^{3+}$	475	Blue	Yellow orange
[Co(CN) <sub>6</sub> ] <sup>3-</sup>	310	Ultraviolet	Pale yellow
$[Cu(H_2O)_4]^{2+}$	600	Red	Blue
$\left[\mathrm{Ti}(\mathrm{H_2O})_6^{}\right]^{3+}$	498	Blue green	Purple

The colour of the absorbed light also depends on the nature of the ligands. For example, Ni2+ ion in [Ni(H<sub>2</sub>O)<sub>6</sub>]<sup>2+</sup> absorbs red and hence has blue green colour. Ni<sup>2+</sup> ion in [Ni(NH<sub>3</sub>)<sub>6</sub>]<sup>2+</sup> ion absorbs yellow colour and is therefore blue in colour. Thus, although the central metal ion is same in both the complex ions, these ions absorb radiation of different colours and therefore have different colours.

# Energy associated with the wavelength of the radiation absorbed can be calculated as follows.

Let  $[M(H_2O)_6]^{n+}$  ion absorbs the radiation of wavelength  $\lambda \mathring{A}$ . Then the frequency or wave number (in cm<sup>-1</sup>) corresponding to this wavelength is given by

Frequency v or wave number (in cm<sup>-1</sup>) of the absorbed radiation of wave length of  $\lambda$ Å.

$$= \frac{1}{\lambda (\text{in Å})} = \frac{1}{\lambda \times 10^{-8} \text{ cm}}$$
$$= \frac{10^8}{\lambda} (\because 1\text{Å} = 10^{-8} \text{cm})$$

This frequency is associated with energy whose magnitude can be calculated in kcal mol<sup>-1</sup> or kJ mol<sup>-1</sup> by using the fact that

 $350 \text{ cm}^{-1} = 1 \text{ kcal mol}^{-1}$ 

and 83.7 cm<sup>-1</sup> =  $1 \text{ kJ mol}^{-1}$ 

1 kcal mol<sup>-1</sup> =  $\frac{?}{}$  cm<sup>-1</sup>

The above conversion is obtained by using the following relation:

$$E = N_{A} h c \bar{v}, \qquad \bar{v} = \frac{E}{N_{A} h c}$$

where 
$$E = 1 \text{ kcal mol}^{-1}$$
 $N_A = 6.02 \times 10^{23} \text{ mol}^{-1}$ 
 $h = 6.6 \times 10^{-34} \text{ Js}$ 
OR
$$h = \frac{6.6 \times 10^{-34} \times 10^{-3}}{4.18} \text{ kcal}$$

$$c = 3 \times 10^8 \text{ ms}^{-1} = 3 \times 10^8 \times 10^2 \text{ cm s}^{-1}$$

$$\overline{v} = \frac{1 \text{ kcal mol}^{-1} \times 4.18}{6.02 \times 10^{23} \text{ mol}^{-1} \times 6.6 \times 10^{-34} \times 10^{-3} \text{ kcals}} = 350 \text{ cm}^{-1}$$

# Therefore, 1 kcal $mol^{-1} = 350 \text{ cm}^{-1}$

 $\times 3 \times 10^{8} \times 10^{2} \,\mathrm{cm \, s^{-1}}$ 

$$1 \text{ kJ mol}^{-1} = \frac{?}{\text{cm}^{-1}} \text{ cm}^{-1}$$

The above conversion is obtained as follows:

$$E = N_A h c \overline{v} \qquad \overline{v} = \frac{E}{N_A h c}$$

where 
$$E = 1 \text{ kJ mol}^{-1}$$

$$N_{A} = 6.02 \times 10^{23} \text{ mol}^{-1}$$

$$h = 6.6 \times 10^{-34} \text{ Js} = 6.6 \times 10^{-34} \times 10^{-3} \text{ kJs}$$

$$c = 3 \times 10^{8} \text{ ms}^{-1} = 3 \times 10^{8} \times 10^{2} \text{ cms}^{-1}$$

$$\bar{v} = \frac{1 \text{ kJ mol}^{-1}}{6.02 \times 10^{23} \text{ mol}^{-1} \times 6.6 \times 10^{-34} \times 10^{-3} \text{ kJs}} \times 3 \times 10^{8} \times 10^{2} \text{ cms}^{-1}$$

$$= 83.7 \text{ cm}^{-1}$$

## Therefore, 1 kJ $mol^{-1} = 83.7 cm^{-1}$

Thus, since  $350 \text{ cm}^{-1} = 1 \text{ kcal mol}^{-1}$ 

$$\frac{10^8}{\lambda} \text{ cm}^{-1} = \frac{10^8}{350 \times \lambda \text{ (in Å)}} \text{ kcal mol}^{-1} \qquad \dots \text{ (i)}$$

Equation (i) shows that

Energy associated with a wavelength of  $\lambda$  Å  $= \frac{10^8}{350 \times \lambda \text{ (in Å)}} \text{ kcal mol}^{-1} \qquad \dots \text{ (ii)}$ 

Similarly, since  $83.7 \text{ cm}^{-1} = 1 \text{ kJ mol}^{-1}$ 

$$\frac{10^8}{\lambda} \text{ cm}^{-1} = \frac{10^8}{83.7 \times \lambda \text{ (in Å)}} \text{ kJ moJ}^{-1} \qquad \dots \text{ (iii)}$$

Equation (iii) shows that

Energy associated with a wavelength of λ Å

$$=\frac{10^8}{83.7\times\lambda\;(\text{in Å})}\;\text{kJ mol}^{-1}\qquad\qquad\dots\text{(iv)}$$

Equations (ii) and (iv) both show that the energy associated with the absorbed radiation is inversely proportional to the wavelength of the radiation but directly proportional to the frequency of the radiation.

# Explanation of the violet (purple) colour of octahedral $[\mathrm{Ti}(\mathrm{H}_2\mathrm{O})_6]^{3+}$ ion by d-d electron transition.

The complex  $[\mathrm{Ti}(\mathrm{H_2O})_6]^{3+}$ , which is violet in colour, is an octahedral complex where the single electron  $(\mathrm{Ti}^{3+}$  is a  $3\mathrm{d}^1$  system) in the metal d orbital is in the ' $t_{2g}$ ' level in the ground state of the complex. The next higher stable state available for the electron is the empty ' $e_g$ ' level. If light corresponding to the energy of yellow-green region is absorbed by the complex, it would excite the electron from ' $t_{2g}$ ' level to the ' $e_g$ ' level ( $t_{2g}^{-1}e_g^{-0} \longrightarrow t_{2g}^{0}e_g^{-1}$ ). Consequently, the complex appears violet in colour). The crystal field theory thus, attributes the colour of the coordination compounds of d-d transition of the electron.

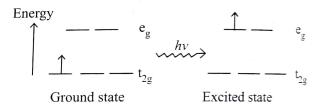


Fig. 7.47 Transition of an electron in  $[Ti(H_20)_6]^{3+}$ 

# b. Colour of the complex ions whose central atom contains empty or completely filled d-orbitals.

The transition metal complex ions whose central atom contains empty ( $d^0$  configuration) or completely filled d-orbitals ( $d^{10}$  configuration) are coloureless. This is due to the fact that in such cases d-d transition is not possible. Thus  $[Sc(H_2O)_6]^{3+}$  ( $d^1$  system),  $[Ti(H_2O)_6]^{4+}$ , ( $d^0$  system),  $[Cu(H_2O)_6]^{\oplus}$ ,  $[Zn(H_2O)_6]^{2+}$  ( $d^{10}$  system) are colourless.

# 7.16 ORGANOMETALLIC COMPOUNDS

Organometallic compounds are the compounds which contain at least one metal carbon bond. They also include the compounds in which C-atom is bonded not only to metal atom but also to metalloids (i.e., element less EN than carbon) e.g., boron (B) silicon (Si), arsenic (As) and tellurium (Te).

However, they are not confined to this definition or to their name. Compounds like carbides, cyanides, carbonates and carbonyls, though they contain metal—carbon bonds are not considered as organometallic compounds by convention, because their properties are much different than those of other compounds belonging to the class of organometallic compounds. For example,  $K_2[Zn(CN)_4]$  and  $[Ni(CO)_4]$ , are coordination compounds but not

organometallic.

Morever, although a compound may contain many hydrocarbon More it is not classified as organometallic when its all the are linked to metal through atoms like O, N or S as in orthoborate, B(OCH<sub>3</sub>)<sub>3</sub>, i.e. H<sub>3</sub>C—O—B < OCH<sub>3</sub>

which is thus not considered as organometallic compounds C-atom is directly linked to boron (B).

CH<sub>3</sub>B(OCH<sub>3</sub>)<sub>2</sub> is an organometallic compound since it

OCH<sub>3</sub>

similarly (C<sub>3</sub>H<sub>7</sub>O)<sub>4</sub>Ti is also not an organometallic compound  $_{\text{MI}}^{\text{Co}} H_5 \text{Ti} (\text{OC}_3 \text{H}_7)_3$  is because it ihas one Ti—C bond.

- 1. Likewise diehtyl zinc,  $(C_2H_5)_2$ Zn is an organometallic compound in which two ethyl groups are directly linked with Zn forming Zn—C bonds.
- 2. Organometallic compounds containing either the hydrocarbon radicals attached to the metal such as (C2H5)4 Pb or containing hydrocarbon radicals along with H atoms attached to the metal such as (CH<sub>3</sub>)<sub>3</sub>SiH are called Simple organometallic compounds whereas those containing at least one hydrocarbon radical along with some others groups attached to metal such as R-Mg-X and  $(C_4H_9)_2SnCl_2$  are called mixed organometallic compounds.
- 3. Organometallic compounds are not found in the nature.

# 1.16.1 CLASSIFICATION OF ORGANOMETALLIC COMPOUNDS

Based on the nature of M—C bond, they are broadly classified into two types as follows:

a. o-bonded organometallic compounds of the main groups (s and p block) elements: These are covalent compounds with (M-C)  $\sigma$  bonds in which bonding consists of localised (M-C)  $\sigma$  bonds formed by sharing of an electrons pairs.

The s- and p-block organometallics are named according to the substituent names used in organic chemistry. For example methylithium for CH<sub>3</sub>Li and trimethylboron for B(CH<sub>3</sub>)<sub>3</sub> which is also called trimethylborane, taking it to be a derivative of its hydrogen counterpart. Thus,  $Si(CH_3)_4$  [(Fig. 7.48(e)] and  $As(CH_3)_3$  [Fig. 7.48(f)] are tetramethylsilane and trimethylarsane respectively.

The oxidation number of the metallic element in an organometallic compound is based on the organic moiety being considered to be anionic. For example, in  $\mathrm{Zn}(\mathrm{CH_3})_2$ and  $CH_3$  group is taken to be negatively charged (1–). Thus, oxidation number of zinc is 2+. The bond in alkyls of s-block elements is highly polar  $(M^{\delta^+}\!\!-\!\!C^{\delta^-})$  in the organometallic compounds of groups 14, 15 and 16, the M-C bonds are of relatively lower polarity. Methyl compounds of Li, Na, Be, Mg and Al are associated through alkyl bridges and

multicentre two electron bonds. The structures of some representative main group organometallic compounds are shown in Fig. 7.48.

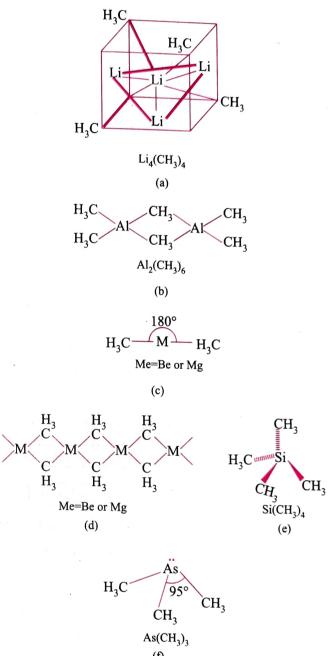


Fig. 7.48 Structures of some representative main group organometallic compounds

Their structures have been represented by empirical formulas though their actual structures are complex.

For example,  $(CH_3)_2$ Be and  $(CH_3)_2$ Mg have bridge structures as represented in Fig. 7.48 (c and d).

Similarly CH<sub>3</sub>Li (methyl lithium) exists as tetramer.

Likewise, (CH<sub>3</sub>)<sub>3</sub>Al (trimethyl aluminium) exists as a dimer in which two methyl groups acts as bridges between two Al-atoms as shown in Fig. 7.48(b).

Organometallic compounds of electropositive metals are strong reducing agents. They are pyrophoric and ignite spontaneously in air.

b. 1.  $\pi$ -bonded organometallic compounds of d and f-block elements –  $\pi$  complexes: Transition metals form organometallic compounds of this type. The formation of these compounds cannot be explained in terms of simple covalent bonding.

**Zeise's salt:** The compound trichloridoetheneplatinate (II),  $[PtCl_3(C_2H_4)]^{\Theta}$  has the structure shown in Fig. 7.49.

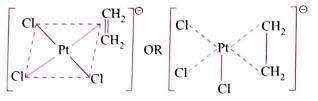


Fig. 7.49 Structures of Zeise's salt  $[PtCl_3(\eta^2-C_2H_4)]^{\bigcirc}$ 

Note: In these compounds the number following  $\eta$ -(eta, the Greek word) represents the number of C-atoms bound to the metal in the compound.

# 2. Sandwich compounds (Ferrocene and dibenzene chromium).

i. The synthesis of highly stable compound Ferrocene [bis-(cyclopentadienyl) iron(II)] or [Fe( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>] (Fig. 7.50) in 1951 was a land mark in the advancement of modern organometallic chemistry. It is called **sandwich compound.** 

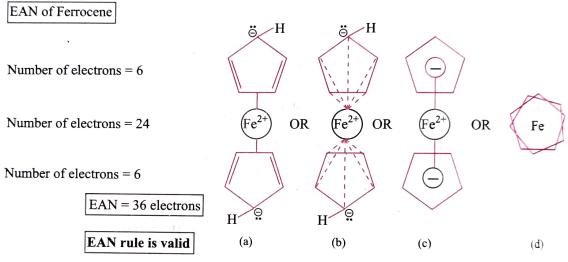


Fig. 7.50 (a–d) Structure of metallocene, Ferrocene [Fe( $C_5H_5$ ) $_2$ ] (OR) [Fe( $\eta^5-C_5H_5$ ) $_2$ ]

Note:  $\eta^5$  represents the number of C-atoms bond to the metal, i.e. 5–C-atoms.

- ii. Ferrocene is composed of  $Fe^{2+}$  sandwiched between two cyclopentadienyl anions and held together by  $\pi$ -complexation. There are no (C–Fe)  $\sigma$ -bonds, as evidenced by the fact that the two rings freely rotate. The most stable conformation is a staggered one with the rings not flush.
- iii. Ferrocene is stable because its Fe<sup>+2</sup> has a full shell of 18 electrons, six of its own (present in its five 3d atomic orbitals) and six from each cyclopentadienyl anion. It also retains the aromaticity of the each cyclopentadienyl anions.
- iv. Many transition metals form sandwich compounds with aromatic compounds providing the combined number of valence shell electrons is 18, e.g. dibenzenechromium  $[Cr(C_6H_6)_2]$  or  $[Cr(\eta^6-C_6H_6)_2]$ , six from Cr, and six from each benzene.

# EAN of Dibenzene chromium

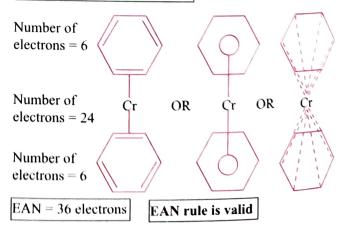


Fig. 7.51 Structure of dibenzene chromium [Cr( $\eta^6$ -C $_6$ H $_6$ ) $_2$ ]

f-Block organometallic compound: In late 1970s, the first f-block organometallic compound was prepared, e.g. [Th<sup>+4</sup> H<sup>-1</sup> (OR)<sup>-1</sup> [η<sup>5</sup> - C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>] or Alkoxohydridobis

(pentamethylcyclopentadienyl) thorium (IV) (Fig. 7.52) the ligand C<sub>5</sub>Me<sub>5</sub>, i.e., pentamethylcyclopentadienyl ion forms stable f-block compounds.

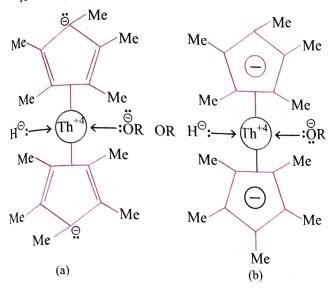


Fig. 7.52 (a-b) Structure of [Th H (OR)  $(\eta^5 - C_5 Me_5)_2$ ]

# 1.16.2 BONDING OF ALKENES TO A TRANSITION METAL

4000 ding to Dewar, the metal to alkene bond consists of two parts:

- i. Overlap of the filled  $\pi$ -orbital of the alkene with an acceptor vacant d-orbital on the metal atom when σ-donation from filled  $\pi$ -orbital of alkene into vacant d-orbital on the metal occurs.
- $\ddot{\mathbf{n}}$ ,  $\pi$  back donation from a filled d-orbital on the metal into vacant antibonding orbital of alkene. Thus according to this view, the metal-alkene bond involves some double bond character Fig. 7.53(a and b).

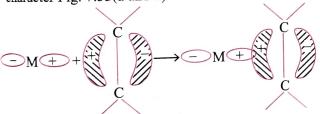


Fig. 7.53 (a)  $\sigma\text{-donation}$  from filled p-orbitals of the alkene into a vacant d-orbital on the metal

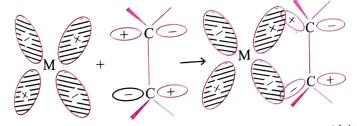


Fig. 7.53 (b)  $\pi$ -back donation from a filled d-orbital on the metal into the vacant antibonding orbital of alkene

# METAL CARBONYLS

A widely studied and important class of organometallic compounds is that of metal carbonyls. The homoleptic carbonyls (compounds Containing carbonyl ligands only) are formed by most of the tansition metals (d metals). The metals constituting the central part of the d block form stable, neutral binary carbonyls like:  $[V\ (CO)_{6}],\ [Cr(CO)_{6}],\ [Mo(CO)_{6}],\ [W(CO)_{6}\ ],\ [Mn_{2}\ (CO)_{10}],$  $[Fe(CO)_5], [Fe_2(CO)_9], [Co_2(CO)_8], [Co_4 (CO)_{12}] [Ni(CO)_4],$ etc. Outside the central part of d-block, the metal carbonyls are usually unstable.

# 7.17.1 CARBONYLS—STRUCTURE AND BONDING

Homoleptic binary metal carbonyls have simple, well-defined structures.

Tetracarbonylnickel(0) is trtrahedral, pentacarbonyliron(o) is trigonal bipyramidal while hexacarbonylchromium(o) is octahedral. Decarbonyldimanganese(o) is made up of two square pyramidal Mn(CO)<sub>5</sub> unit joined by a Mn-Mn bond. Octacarbonyldicobalt(o) has a Co-Co bond bridged by two CO groups (Fig. 7.54).

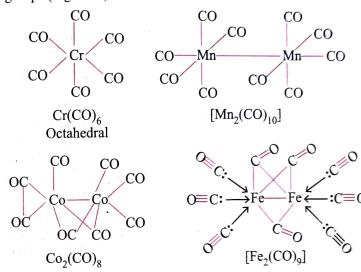


Fig. 7.54 Structure of some representative homoleptic metal

### 7.17.2 PROPERTIES OF METAL CARBONYLS

- i. Most of the metal carbonyls are solids at room temperature and atmospheric pressure. The only exceptions are nickel and iron carbonyls which are liquids.
- ii. Mononuclear carbonyls are volatile and toxic. Further, they are either colourless or they have a light colour. For example Fe(CO)<sub>5</sub> is light-staw coloured liquids. On the other hand, polynuclear carbonyls have a deep colour. Fe<sub>3</sub>(CO)<sub>12</sub>, dodecarcarbonyl triiron(0), for example is a deep grass green solid.
- iii. They are soluble in hydrocarbon solvents, the only exception being Fe<sub>2</sub> (CO)<sub>9</sub>, i.e., enneacarbonyl diiron(0).
- iv. Their reactivity is partly due to the central (metal atom and partly due to the CO ligands.

# 7.17.3 USES OF METAL CATALYSTS

- i. They are used as industrial catalysts.
- ii. They are used as precursors in synthesis of organic compounds.

## 7.17.4 BONDING IN METAL CARBONYLS

The metal-carbon bonds in metal carbonyls have both  $\sigma$  and  $\pi$ character. The formation of bonds between the metal and carbon atom of carbon monoxide is described below.

The first overlap takes place between the filled bonding  $\pi_{2p}$ orbital of the carbon monoxide with an empty metal d-orbital resulting in a  $\sigma$ -bond between the metal and carbon atom of carbon monoxide. Here, donation of lone pair of electrons on carbon into a vacant d-orbital of the metal takes place. As CO is a weak base/ weak donor, the  $\sigma$ -bond formed with the metal atom is weak.

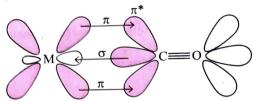


Fig. 7.55 (a)  $\sigma$ -overlap. Donation of lone pair of electrons on C-atom into a vacant d-orbitals on the metal, i.e. formation of (M–C)  $\sigma$ -bond (b)  $\pi$ -overlap. Donation of electrons from a filled metal d-orbitals into a vacant antibonding  $\pi^*$ -orbital of CO, i.e., formation of (M–C)  $\pi$  bond

The second overlap takes place between the filled metal d-orbital with an empty antibonding  $\pi_{2p}^*$  orbital of the carbon monoxide resulting in additional  $\pi$  bond between the metal and same carbon monoxide molecule. Here, donation of electrons from a filled metal d-orbital into a vacant antibonding  $\pi^*$ -orbital of CO occurs (back bonding). Here, CO is acting as an acceptor ligand.

The effect of  $\sigma$  bond formation strengthens  $\pi$  bond and vice versa. This is called synergic effect (i.e., working together towards the same goal). Thus, as a result of synergic effect, the bond between CO and metal is strengthened.

Further, as explained above, a weak a bond is formed by donation of electron pair from carbon to metal ( $M \leftarrow C \equiv 0$ ) and a stronger  $\pi$  bond (second bond) is formed by back donation of electrons from filled d-orbital of metal into empty antibonding  $\pi^*$  orbital of carbon ( $\pi$  M  $\rightarrow$  C bond). The total bonding is thus M = C = C). Thus, bond order of C - O) bond is reduced from triple bond to double bond. This is supported by the fact that (C - O) bond length in C = 0 is 128 Å and it increases to about 1.15 Å in many carbonyls.

Ligands such as CO which are capable of accepting an appreciable amount of electron density from the metal atom into empty  $\pi$  or  $\pi^*$  orbital of their own are called  $\pi$ -acceptor or  $\pi$ -acid ligands.

# 7.18 PREPARATION OF **COORDINATION COMPOUNDS**

Coordination compounds are prepared by the following general methods of preparation:

- 1. Direct combination of reactants: Under suitable conditions, the reactants are made to react in requisite molecular proportion to produce coordination compounds. For example,
  - Metal ammines can be obtained by the direct reaction between a metal salt and liquid ammonia.

$$NiCl_2(s) + 6NH_3(l) \longrightarrow [Ni(NH_3)_6]Cl_2$$

ii. Reaction between ethylenediamine (en) and PtCl<sub>2</sub> give<sub>8</sub> [Pt(en),]Cl<sub>2</sub>.

$$NiCl_2 + 2 en \longrightarrow [Pt(en)_2]Cl_2$$

2. Substitution reactions: Most of the coordination compounds are prepared by this method. In this method stronger ligands replace the weaker ligands. For example, stronger figure  $[Cu(NH_3)_4]^{2+}$  complex ion in prepared by heating  $aqueou_S$ copper sulphate solution with ammonia.

$$[Cu(H_2O)_4]^{2^+} + 4NH_3 \longrightarrow [Cu(NH_3)_4]^{2^+} + 4H_2O$$
  
In this case, NH<sub>3</sub> molecules replace the water molecules (weaker ligands) surrounding the Cu<sup>2+</sup> ion.

3. Redox reactions: By this method, a complex with the metal atom in a higher oxidation state than in the starting material is obtained by carrying out the process of complex formation in the presence of an oxidising agent e.g. H<sub>2</sub>O<sub>2</sub> or perchlorates. For example pentraamminitratocobalt (III) nitrate [Co(NO<sub>3</sub>)(NH<sub>3</sub>)<sub>5</sub>] (NO<sub>3</sub>)<sub>2</sub> is prepared by adding concentrated solution of ammonia containing NH<sub>4</sub>NO<sub>2 to</sub> cobalt (II) nitrate solution in the presence of H<sub>2</sub>O<sub>2</sub>.

$$2[\text{Co(H}_2\text{O)}_6] (\text{NO}_3)_2 + 8\text{NH}_3 + 2\text{NH}_4\text{NO}_3 + \text{H}_2\text{O}_2 \longrightarrow \\ 2[\text{Co(NO}_3) (\text{NH}_3)_5] (\text{NO}_3)_2 + 14\text{H}_2\text{O}_3 + 14$$

Similarly, hexaammininecobalt (III) chloride can be prepared by adding ammonium chloride to the aqueous solution of cobalt chloride made alkaline with ammonia in the presence of H<sub>2</sub>O<sub>2</sub>.

$$2\text{CoCl}_{2} + 2\text{NH}_{4}\text{Cl} + 10\text{NH}_{3} + \text{H}_{2}\text{O}_{2} \longrightarrow 2[\text{Co(NH}_{3})_{6}] \text{Cl}_{3} + 2\text{H}_{2}\text{O}_{2}$$

- a. Preparation of σ-bonded organometallic compounds:
  - Organoalkali compounds and Grignard reagents: These are obtained directly by the reaction between an alkyl halide and metal e.g.,

$$R - X + 2M \xrightarrow{\text{ether}} R - M + MX$$

$$R - X + Mg \xrightarrow{\text{ether}} R - M - MX$$

$$(M = Li, Na, K, X = Cl, Br, I)$$

Tetraalkyl tin and tetraalkyl lead: These are obtained by reaction of metal halide with organometallic compound.

$$SnCl_4 + 4BuLi \longrightarrow Bu_4Sn + 4LiCl$$
Butyl lithium Tetrabutyl tin

$$\begin{array}{ccc} PbCl_4 & + & 4EtMgBr & \longrightarrow & Et_4Pb + 4MgBrCl \\ & & Ethyl \; mag \; bromide & Tetraethyl \\ & & & (G.R.) & lead \; (TEL) \end{array}$$

Tetraethyl lead (TEL) which is an important anti-knocking agent is prepared commercially by reaction of ethyl iodide with lead sodium alloy.

4C<sub>2</sub>H<sub>5</sub>I + 4 Pb/Na 
$$\longrightarrow$$
 (C<sub>2</sub>H<sub>5</sub>)<sub>4</sub>Pb + 4NaI + 3Pb

# preparation of $\pi$ -complexes:

i. Preparation of Zeise's salt: It is obtained by direct replacement of the weaker Cl<sup>©</sup> ligand of [PtCl<sub>4</sub>]<sup>2-</sup> complex ion by ethylene on heating.

$$K_2[PtCl_4] + CH_2 = CH_2 \xrightarrow{\Delta} K_3[PtCl_3(C_2H_4)] + KCl$$

Zeise's salt

**ji. Preparation of ferrocene:** It is obtained by the following reaction:

$$2C_5H_5MgBr + FeCl_2 \longrightarrow [(C_5H_5)_2Fe] + 2MgBrCl$$
  
Ferrocene

iii. Preparation of dibenzene chromium: It is obtained by heating benzene with chromium vapours:

$$2C_6H_6 + Cr \text{ (vapour)} \longrightarrow [(C_6H_6)_2Cr]$$

c. Preparation of metal carbonyls: Metal carbonyls are obtained by direct reaction between the metal and carbon monoxide under appropriate condition e.g.,

$$Ni + 4CO \xrightarrow{\text{Room Temp.}} [Ni(CO_4)]$$

$$Nickel \text{ tetracarbonyl}$$

$$Fe + 5CO \xrightarrow{\text{Heat}} [Fe(CO)]$$

Fe + 5CO 
$$\xrightarrow{\text{Heat}}$$
 [Fe(CO)<sub>5</sub>] Iron pentacarbonyl

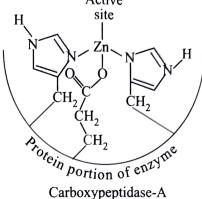
The reaction between nickel and carbon monoxide to form volatile compounds which decomposes easily to give back nickel is used for the purification of nickel. The method is known as **Mond's process.** 

# 19 IMPORTANCE AND APPLICATIONS OF COORDINATION COMPOUNDS/COMPLEXES

ne importance of coordination compounds in various fields is scussed below:

# 1. In biological systems:

- **a.** Coordination compounds are of great importance in biological systems. Familiar examples being:
  - i. Chlorophylls (the green pigments in plants, central to photosyntyhesis).
  - ii. Haemoglobin (the red pigment of blood, which acts as oxygen carrier) along with myoglobin (which stores oxygen and is a regulator of respiration).
  - iii. Vitamin B<sub>12</sub> cyanocobalammine, the anti-pernacious anaemia factor.
    - All of these, respectively, are the coordination compounds of magnesium, iron and cobalt with the macrocyclic porphyrin and corrin ligands.
- b. Among the other compounds of biological importance with coordinated metal ions are the enzymes like, carboxypeptides A and carbonic anhydrase (catalysts of biological system) (Figure).



$$\begin{bmatrix} B_{12} \Rightarrow \text{Central metal atom (CMA)} = \text{Co}^{2+} \\ \text{Ligand} = \text{Corrin} \\ \text{(c)} \end{bmatrix}$$

(b)

Heme B found in haemoglobin and myoglobin. Central metal atom (CMA) = Fe<sup>2+</sup> Ligand = Porphyrin

(d)

Chlorophyll (a and b) central metal atom (CMA) = Mg<sup>2-1</sup> Ligand = Porphyrin

(e)

### Structures of some important compounds

### 2. In analytical chemistry:

- a. In qualitative analysis: In salt analysis, the presence of a number of basic radicals is confirmed by converting them into suitable complexes which are coloured. For example
  - i. Fe<sup>2+</sup> and Fe<sup>3+</sup> ions are tested and distinguished by potassium ferrocyanide K<sub>4</sub>[Fe(CN)<sub>6</sub>] and potassium ferricyanide K<sub>3</sub>[Fe(CN)<sub>6</sub>] as shown below:

	Reagent	Fe <sup>2+</sup>	Fe <sup>3+</sup>
i.	[Fe <sup>2+</sup> (CN) <sub>6</sub> ] <sup>4-</sup>	Fe <sub>2</sub> <sup>2+</sup> [Fe <sup>2+</sup> (CN) <sub>6</sub> ] <sup>4-</sup>	Fe <sub>4</sub> <sup>3+</sup> [Fe <sup>2+</sup> (CN) <sub>6</sub> ] <sub>3</sub> <sup>4-</sup>
	Ferrocyanide	Ferro-ferro cyanide	Ferri–ferro cyanide
	ion	(white ppt)	(Prussion blue)
ii.	[Fe <sup>3+</sup> (CN) <sub>6</sub> ] <sup>3-</sup>	Fe <sub>3</sub> <sup>2+</sup> [Fe <sup>3+</sup> (CN) <sub>6</sub> ] <sub>2</sub> <sup>3-</sup>	Fe <sup>3+</sup> [Fe <sup>3+</sup> (CN) <sub>6</sub> ] <sup>3-</sup>
	Ferricyanide	Ferro–ferri cyanide	Ferri-ferri cyanide
	ion	(Turnbull's blue)	(Brown solution)

Note: However, Prussian blue and Turnbull's blue are chemically identical. They are mainly a mixture of ferric potassium ferrocyanide, Fe<sup>III</sup>K[Fe<sup>III</sup>(CN)<sub>6</sub>] and ferrous potassium ferricyanide, Fe<sup>III</sup>K[Fe<sup>III</sup>(CN)<sub>6</sub>] with some ferric ferrocyanide, Fe<sub>4</sub><sup>III</sup>[Fe<sup>III</sup>(CN)<sub>6</sub>]<sub>3</sub> and ferroferriccyanide, Fe<sub>3</sub><sup>II</sup>K[Fe<sup>III</sup>(CN)<sub>6</sub>]<sub>2</sub>. Fe<sup>3+</sup> ion partially oxidises [Fe<sup>III</sup>(CN)<sub>6</sub>]<sup>4-</sup> forming some [Fe<sup>III</sup>(CN)<sub>6</sub>]<sup>3-</sup>. Thus KFe<sup>II</sup>[Fe<sup>III</sup>(CN)<sub>6</sub>] is formed.

ii. Fe<sup>3+</sup> ions are also detected by adding thiocyanate ions (from ammonium thiocyanate) when a blood red colouration is obtained due to the formation of a complex i.e. ferrithiocyanate.

$$Fe^{3+} + 3CNS^{\odot} \longrightarrow Fe(CNS)_3$$

Thiocyanate ion Ferrithiocyanate (blood red colour)

iii. Zn<sup>2+</sup> ions are tested by adding potassium ferrocyanide solution to the acidified salt solution when a **bluish white precipitate** is obtained due to formation of a complex i.e., zinc ferrocyanide or zinc hexacyanoferrate (II).

$$2ZnCl_2 + K_4[Fe(CN)_6] \longrightarrow Zn_2[Fe(CN)_6] + 4KCl$$
Zinc hexacyano
ferrate(II)
(Bluish white ppt.)

OR  

$$\operatorname{Zn}^{2^+} + [\operatorname{Fe}^{2^+}(\operatorname{CN})_6]^{4^-} \longrightarrow \operatorname{Zn}_2[\operatorname{Fe}(\operatorname{CN})_6]$$

iv. Cu<sup>2+</sup> ions are tested by adding potassium ferrocyanide solution to the acidified salt solution when a chocolate colour precipitate is obtained due to formation of a complex i.e., copper ferrocyanide or copper hexacyanoferrate (II).

$$Cu^{2^+} + [Fe(CN)_6]^4 \longrightarrow Cu_2[Fe(CN)_6]$$

Chocolate colour precipitate

v. a. The presence of Co<sup>2+</sup> ion is tested by potassium ferricyanide test when a reddish brown precipitate is obtained due to the formation of an insoluble complex.

$$3\text{CoCl}_2 + 3\text{K}_3[\text{Fe(CN)}_6] \xrightarrow{\text{warm}} \text{Co}_3[\text{Fe(CN)}_6]_2 + 6\text{KCl}$$
Potassium Cobalt hexacyano ferrate (III) (reddish brown ppt.)

OR

$$3\text{Co}^{2+} + [\text{Fe}^{3+}(\text{CN})_6]^{3-} \xrightarrow{\text{warm}} \text{Co}_3[\text{Fe}(\text{CN})_6]_2$$

**b.** Co<sup>2+</sup> ions are also tested by adding ammonium thiocyanate solution when a blue colour is obtained due to formation of a complex.

$$\begin{array}{c} \operatorname{CoCl_2} + \operatorname{NH_4SCN} \xrightarrow{\quad \text{warm} \quad} \operatorname{Co(SCN)_2} + 2\operatorname{NH_4Cl} \\ & \downarrow 2\operatorname{NH_4SCN} \\ & (\operatorname{NH_4)_2}[\operatorname{Co(SCN)_4}] \\ & \text{Ammonium tetrathiocyanatocobaltate(II)} \\ & (\text{blue colour}) \end{array}$$

OR
$$Co^{2+} + 2SCN^{\Theta} \longrightarrow [Co(SCN)_2] \xrightarrow{2SCN^{\Theta}} [Co(SCN)_4]^{2-}$$

vi. Separation of mixture of two ions: A mixture of two ions can be separated also. Some reagent under

the same conditions, one of the metal ions may form a soluble complex while the other may form as insoluble complex.

For example, with ammonium or potassium ferrocyanide solution, Co<sup>2+</sup> ion forms an insoluble complex while Ni<sup>2+</sup> ion forms similar complex but soluble in NH<sub>4</sub>OH.

i. 
$$\operatorname{Co}^{2+} + [\operatorname{Fe}(\operatorname{CN})_6]^4 \longrightarrow \operatorname{Co}_2[\operatorname{Fe}(\operatorname{CN})_6]$$
Insoluble in NH<sub>4</sub>OH

Insoluble in 
$$NH_{4OH}$$

ii.  $Ni^{2+} + [Fe(CN)_{6}]^{4-} \longrightarrow Ni_{2}[Fe(CN)_{6}]$ 
Soluble in  $NH_{4OH}$ 

and yearmples of the use of coordination compounds in qualitative and quantitative chemical analysis. The familiar colour reaction given by metal ions with a number of ligands (especially the chelating ligands as a result of formation of coordination entities, form the basis for their detection and estimation by classical and instrumental methods of analysis. Most of these reactions are highly specific and sensitive under controlled experimental conditions. Often the detection/estimation limits tend to parts per million (ppm), or even parts per billion (ppb) levels.

Familiar examples of such reagents are as follows: dimethylglyoxime, α-nitroso-β-naphthol, 8-hydroxyquinoline, 1, 10-phenanthroline (ph), benzoin oxime (i.e. cupron), as given in following Table 7.25.

**Table 7.25** Colour of metal ions with chelating (organic) reagents

	Metal ion to be estimated	Colour	рН	Organic or chelating reagents used
i.	Ni <sup>2+</sup>	Red	9–10	Dimethylglyoxime
ii.	Co <sup>2+</sup>	Red precipitate		α-Nitroso-β-naphthol
iii.	Al <sup>3+</sup>	Blue	-	8-hydroxyquinoline (oxine)
iv.	Fe <sup>3+</sup>	Brown	-	1,10-Phenanthroline (ph)
v.	Cu <sup>2+</sup>	Red	9–10	Benzoin oxime (i.e., cupron)

**Note:** In ammonical buffer, oxine (8-hydroxyquinoline forms yellow precipitate with Mg<sup>2+</sup> ion.

i. Ni<sup>2+</sup> ions: The presence of Ni<sup>2+</sup> ion is detected by adding dimethyl glyoxime in the presence of NH<sub>4</sub>OH (at pH =

9-10) to the salt solution, a red ppt. is formed, due to formation of a complex.

$$2 \begin{pmatrix} H_{3}C - C = N.OH \\ H_{3}C - C = N.OH \end{pmatrix} + Ni^{2+} + 2OH \underline{pH} = 9-10$$

$$OH - - - - O$$

$$H_{3}C - C = N$$

$$OH - - - - O$$

$$H_{3}C - C = N$$

$$N = C - CH_{3}$$

$$N$$

ii. The presence of  $Co^{2+}$  ion is detected by adding  $\alpha$ -nitroso- $\beta$ -naphthol to the salt solution, a red ppt. is formed due to the formation of a complex.

$$O=N$$
:
$$2$$

$$α-nitroso-β-naphthol$$

$$N:$$

$$O=Co^{2+}$$

$$N:$$

$$Co^{2+}$$

$$N:$$

$$Red precipitate$$

iii. Al<sup>3+</sup>: The presence of Al<sup>3+</sup> ion is detected by adding 8-hydroxyquinoline to the salt solution, a blue precipitate is formed due to the formation of a complex.

iv. Fe<sup>3+</sup>: The presence of Fe<sup>3+</sup> ion is detected by adding 1, 10-phenanthroline (ph) to the salt solution, a brown precipitate is formed due to the formation of a complex.

benzoin oxime (also called as cuperon) in the presence of NH<sub>4</sub>OH (at pH = 9-10) to the salt solution, a red precipitate is formed due to the formation of a complex.

$$2 \left(\begin{array}{c} Ph-C=N.OH \\ Ph-C=N.OH \end{array}\right) + Cu^{2+} + 2 \stackrel{\ominus}{OH} \stackrel{pH=9-10}{\longrightarrow}$$

$$2H_2O + \left[\begin{array}{c} OH-----O \\ Ph-C=N: \\ N=C-Ph \\ O-----HO \\ Red precipitate \end{array}\right]$$

# 4. In quantitative analysis (estimations):

- i. Gravimetric analysis: The amount of metal present in a given sample can be estimated by converting a known amount of the sample into an insoluble complex which can be filtered, dried and weighed. For example, the amount of nickel present in a salt is estimated by precipitating it as nickel dimethyl glyoxime complex.
- ii. Volumetric analysis (complexometric titrations): A number of metal ions react completely with polydentate ligands at an appropriate pH to form complexes. Hence, the solutions of metal ions can be titrated against the solutions of the polydentate ligands in the presence of a buffer (NH<sub>4</sub>OH + NH<sub>4</sub>Cl) at-pH = 10 and the end point can be detected by using a suitable indicator (eriochrome black-T). The colour must be wine red at this stage. The colour at the end point is blue. The most common polydentate ligand used is ethylene diamine tetraacetic acid (EDTA) is as given.

It is a hexadentate ligand and it coordinates through two N-atoms and four O-atoms of the —COOH groups. It is usually represented by  $H_4Y$ . Its disodium salt is commonly used because of its better solubility in water. Its formula is represented as  $Na_2H_2Y$ . It ionises as

$$Na_2H_2Y \longrightarrow 2Na^{\oplus} + H_2Y^{2-}$$

The reactions of the metal ions like Ca<sup>2+</sup>, Mg<sup>2+</sup>, Zn<sup>2+</sup> ions etc. (in general, M<sup>2+</sup>) with EDTA may be represented as follows:

$$M^{2+} + H_2Y^{2-} \Longrightarrow MY^{2-} + 2H^{\oplus}$$

The indicators most commonly used are organic dyes such as Eriochrome black-T or Calcon.

The hardness of water due to presence of Ca<sup>2+</sup> and Mg<sup>2+</sup> ions is estimated by these complexometric titration.

- iii. In metallurgy (extraction of metals): The noble metals like silver (Ag) and gold (Au) are extracted from their ores through the formation of cyanide complexes  $[Ag(CN)_2]^{\Theta} [Au(CN)_2]^{\Theta}$  respectively.
  - a. Extraction of silver (Ag): Silver is extracted from its ore by first dissolving the ore in NaCN solution and then precipitating out silver by adding more reactive electropositive metal, zinc (Zn).

i. 
$$Ag_2S + 4NaCN \Longrightarrow 2Na[Ag(CN)_2] + Na_2S$$
  
Sodium dicyano  
argentate (I)  

$$\downarrow Zn$$

$$Na_2[Zn(CN)_4] + 2Ag$$

OR
ii. 
$$4Ag^{\oplus} + 4CN^{\ominus} \longrightarrow 2[Ag(CN)_2]^{\ominus}$$

$$\downarrow Zn$$

$$[Zn^{2+}(CN^4)_4]^{2-} + 2Ag$$

iii. Native silver (Ag) also dissolve in NaCN solution in the presence of O<sub>2</sub> in air. Silver is precipitated by addition of scrap zinc (Zn).

$$4Ag + 8NaCN + O_2 \text{ (from air)} + 2H_2O$$

$$\downarrow Zn$$

$$Na_2[Zn(CN)_4] + 2Ag \stackrel{Zn}{\longleftarrow} 4Na[Ag(CN)_2] + 4NaOH$$

b. Extraction of gold (Au): The cyanide process used for the extraction of gold is based upon the fact that gold dissolves in KCN solution in the presence of atmospheric oxygen to form a soluble cyanide complex

$$4Au + 8KCN + 2H2O + O2(air) \longrightarrow 4K[Au(CN)2] + 4 KOH$$

From the complex cyanide solution, gold is precipitated out by adding zinc scraps.

$$2K[Au(CN)_2] + Zn \longrightarrow K_2[Zn(CN)_4] + 2Au$$

6. In purification of metals: Some metals are purified by formation of their metal carbonyls followed by their decomposition, e.g., impure nickel is converted into nickel tetracarbonyl Ni(CO)<sub>4</sub> which on decomposition gives pure nickel. This method is known as Mond's process.

## 7. In industry:

- a. As catalysts: Coordination compounds are used as catalysts for many industrial processes. A few examples are given below:
  - i. Homogeneous catalysis: Wilkinson catalysts, with the formula, [RhCl (Ph<sub>3</sub>P)<sub>3</sub>], i.e., chloridotris (triphenyl) rhodium (I), is used for selective hydrogenation of alkene. The double bond at the end of the chain is hydrogenated but the double bonds elsewhere in the chain are not affected. Moreover, Wilkinson catalyst (WC) also reduces carboxylic acids (RCOOH) to alcohols (RCH<sub>2</sub>OH), e.g.,

$$CH_3CH_2CH=CH_2 \xrightarrow{WC} CH_3CH_2CH_2CH_3$$

$$CH_3CH=CH-CH_3 \xrightarrow{WC} No reaction$$

$$CH_3COOH \xrightarrow{WC} H_3C-CH_2OH$$

- ii. Heterogeneous catalysis: Ziegler-Natta catalyst is used as heterogeneous catalysts, e.g., triethylaluminium [(C<sub>2</sub>H<sub>5</sub>)<sub>3</sub>Al] and titanium tetrachloride (TiCl<sub>4</sub>). It is used as a catalyst for the low temperature polymerisation of alkene i.e., for the synthesis of HDPE (high density polyethene) from ethene.
- b. In electroplating: Articles can be electroplated with silver or gold much more smoothly and evenly from solutions of the complexes  $[Ag(CN)_2]^{\Theta}$  and  $[Au\ (CN)_2]^{\Theta}$  than from the solutions of simple metal ions.
- c. In photography: The developed film is fixed by washing with hypo solution which dissolves the undecomposed AgBr to form a complex.

$$\begin{array}{c} AgBr + 2Na_2S_2O_3 \xrightarrow{\cdot} Na_3[Ag(S_2O_3)_2] + NaBr \\ Sod. \ dithiosuiphato \\ argentate \ (I) \end{array}$$

- d. As dyes or pigments: Phthalocyanine blue which is an extremely stable complex of copper (II) is one of the many complex compounds used as dyes or pigments.
- 8. In medical field: The well-known examples are given below:
  - i. British anti-Lewisite (BAL) in which the chelating agent is HSCH<sub>2</sub>CH(SH)CH<sub>2</sub>OH was developed during war time as an antidote to an arsenic containing poisonous

gas (Lewisite). BAL is now used to treat poisoning by As, Hg, Au, Bi, Sb and even Pb and Cd.

- Calcium salt of EDTA is quite often used for treatment of lead poisoning and dermatitis and poisoning by Cr or Ni.
- iii. Metals present in toxic proportions in animals and plants are removed by chelate therapy, e.g., excess ol copper and iron are removed by using chelating ligands, D-penicillamine and desferrioxime-B.
- iv. Recently, the platinum complex, cis [Pt(NH<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>], known as cisplatin has been found to be useful in the treatment of cancer (tumours). Its structure is as follows:

This compound has the ability to block the uncontrolled division of cancerous cells that results in the growth of tumours. Recent studies show that cis-platin can cause serious side effect, including severe kidney damage. Therefore now-a-days cis-platin has been replaced by the following compound.

$$\begin{bmatrix} Cl & NH_3 & H_3N & Pt \\ H_3N & NH_2 - (CH_2)_n - H_2N & NH_3 \end{bmatrix}$$
trans-isomer (n = 2 to 6)

- v. A number of organoarsenic compounds are used as main remedy for syphilis.
- vi. The modern surgery makes use of silicon rubbers for spare parts in the body.
- vii. Silicon rubbers are also used as cosmetic surgery.
- 9. In agriculture: To prevent infection of young plants, the seeds are treated with organometallic compounds such as ethyl mercury iodide (C<sub>2</sub>H<sub>5</sub>HgI).
- 10. Organic synthesis: They are widely used in the synthesis of various types of organic compounds, e.g., organolithium and organomagnesium compounds (Grignard reagent) are commonly used for the synthesis of different types of organic compounds.
- 11. Future applications: It is expected that the organometallic compounds will find an important role in the production of semiconductors for the electronic industry, pharmaceuticals, flavours and fragrances.

# CONCEPT APPLICATIONS EXERCISE 7.3

- 1. Find out the total number of compound(s) which is/are diamagnetic in nature according to CFT.
  - I.  $Na_3[Cr(OX)_3]$
- II.  $Na_3[Co(CN)_6]$
- III. Ca[NiBr<sub>4</sub>]
- IV. Cl,O

- V. ClO, VI. ClO<sub>3</sub> VII. Cl,O7.
- 2. Calculate total C.F.S.E. in term of Dq for the complex [MnCl<sub>6</sub>]<sup>3-</sup> and [FeBr<sub>6</sub>]<sup>4-</sup>
- 3. If x = C.F.S.E. value of light pink coloured compound formed when KMnO<sub>4</sub> is reduced by acidified H<sub>2</sub>S. y = C.F.S.E. value of light-pink coloured compound (A) formed is the reaction.

A (Light pink colour complex) 
$$\xrightarrow{Pb_3O_4/\text{dif. HNO}_3} \xrightarrow{\Delta}$$

$$HMnO_4 \xrightarrow{H_2S/H^{\oplus}} A$$
 (Light pink colour compound)

Then calculate the value of (x - y).

- 4. C.F.S.E. for  $[Co(H_2O)_6]^{2+}$  is 6400 cm<sup>-1</sup>, pairing energy for  $\text{Co}^{2+}$  is 20,000 cm<sup>-1</sup>, then calculate the value of  $\frac{\emptyset_0}{1-1}$ in cm<sup>-1</sup>.
- 5. If x = number of  $\pi$ -bonds in ferrocene y = Number of  $\pi$ -bonds in zeise's salt z = Number of  $\pi$ -bonds is dibenzene chromium. Then (x + y) - z is:
- 6. Calculate the total number of  $\sigma$ ,  $\pi$  and  $\delta$ -bond in the complex anion [Re<sub>2</sub>Br<sub>8</sub>]<sup>2</sup>

# Solved Examples

# EXAMPLE 7.1

Three compounds A, B and C have empirical formula CrCl<sub>3</sub>·6H<sub>2</sub>O. When 1 g of A was kept in a container with dehydrating agent. it lo st water content and attained constant weight of 0.865 g. When 1 g of B was kept in that vessel, it attained a constant weight of 0.932 g. Compound C showed no loss in water content.

- a. Find the composition of A, B and C.
- b. If an excess of aqueous AgNO<sub>3</sub> solution is added to 1g solution of A, B and C, what amount of AgCl will be precipitated in each case.

## Sol.

a. Molecular mass of CrCl<sub>3</sub>·6H<sub>2</sub>O

$$= 52 + 35.5 \times 3 + 6 \times 18 = 266.5 g$$

1 g of A gives (1 - 0.865) g = 0.135 g of  $H_2O$  on dehydration  $\therefore$  266.5 g of A gives = 0.135 × 266.5 g  $\approx$  36.0 g of H<sub>2</sub>O This weight of 36 g shows that on dehydration A gives two moles of  $H_2O$  (molecular mass of  $H_2O$ ) =  $1 \times 2 + 16 = 18$  g), i.e., two moles of H<sub>2</sub>O are present outside the coordination sphere in the composition of A. Thus the composition of A is given by

A = 
$$[Cr(H_2O)_4Cl_2]Cl \cdot 2H_2O$$
  
On similar grounds it can be shown that:  
266.5 g of B will give  $(1 - 0.932) \times 266.5$   
or 18.122 g of  $H_2O$ .

This weight (=18.122 g) corresponds to one mole of  $H_2O$ . Thus B has one H<sub>2</sub>O mole outside the coordination sphere and hence the composition of B is given by

$$B = [Cr(H_2O)_5Cl]Cl_2 \cdot H_2O$$

Since C shows no loss in water content, no H<sub>2</sub>O molecule is outside the coordination sphere, i.e., all the six H<sub>2</sub>O molecules are inside the coordination sphere and hence the composition of C is given by

$$C = [Cr(H_2O)_6]Cl_3$$

**b.** Molecular mass of AgCl = 108 + 35.5 = 143.5 g

Since A, i.e., [Cr(H<sub>2</sub>O)<sub>4</sub>Cl<sub>2</sub>]Cl·2H<sub>2</sub>O on treatment with AgNO3 solution, gives one AgCl mole,

∴ 266.5 g of A gives 143.5 g of AgCl

:. 1 g of A gives 
$$\frac{143.5}{266.5}$$
 g = 0.53 g of AgCl

Since B, i.e., [Cr(H<sub>2</sub>O)<sub>5</sub>Cl]Cl<sub>2</sub>·H<sub>2</sub>O gives two moles of AgCl.

266.5 g of B gives 2 × 143.5 g of AgCl

:. 1 g of B gives 
$$\frac{2 \times 143.5}{266.5}$$
 g = 1.076 g of AgCl

Since C, i.e., [Cr(H<sub>2</sub>O)<sub>6</sub>]Cl<sub>3</sub> gives three moles of AgCl.

266.5 g C gives 3 × 1435 g of AgCl.

:. 1 g of C gives 
$$\frac{3 \times 143.5}{266.5}$$
 g = 1.614 g of AgCl

### EXAMPLE 7.2

How many isomers are possible for the complex ion [Cr(NH<sub>2</sub>) (OH),Cl<sub>3</sub>]<sup>2-</sup>?

Sol. It is an example of (Ma<sub>3</sub>b<sub>2</sub>c]<sup>n±</sup> type and 3 isomers are possible as shown below:

 $H_3N$ 

Cl-Cl ⇒ cis

Cl-Cl ⇒ cis and trans

Cl-OH ⇒ cis

 $Cl-OH \Rightarrow cis and trans$ 

 $OH-OH \Rightarrow cis$ 

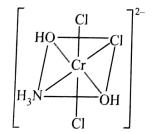
 $OH-OH \Rightarrow cis$ 

**(I)** 

 $C1-NH_3 \Rightarrow cis$  and trans  $NH_3-OH \Rightarrow cis$  and trans

 $NH_3$ -OH  $\Rightarrow$  cis

(II)



 $Cl-Cl \Rightarrow cis and trans$ 

Cl-OH ⇒ cis

OH–OH ⇒ trans

 $NH_3$ -OH  $\Rightarrow$  cis

(III)

### EXAMPLE 7.3

For the square planar complex [Pt(NH<sub>3</sub>)<sub>4</sub>(NH<sub>2</sub>OH) py (NO<sub>2</sub>)] $^{\oplus}$ , how many geometrical isomers are possible?

Sol. It is an example of [Mabcd]<sup>n±</sup> type. Three geometrical isomers are possible for the above compound.

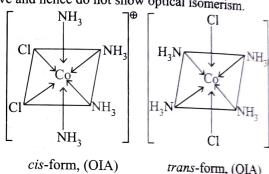
### EXAMPLE 7.4

Give the total number of geometrical and optical isomers given by:

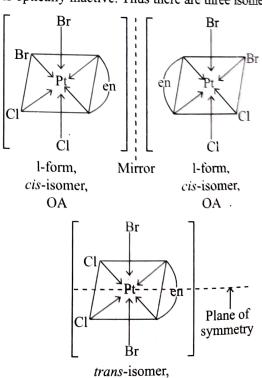
- [Co(NH<sub>3</sub>)<sub>4</sub>Cl<sub>2</sub>]<sup>€</sup>
- ii. [Pt(en)Br<sub>2</sub>Cl<sub>2</sub>]
- iii. [CrCl<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>]

### Sol.

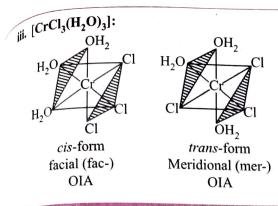
i. [Co(NH<sub>3</sub>)<sub>4</sub>Cl<sub>2</sub>]<sup>⊕</sup>: This ion is an octahedral complex ion of [Ma<sub>4</sub>b<sub>2</sub>] type and hence has cis and trans isomers (two geometrical isomers). Both these isomers are optically inactive and hence do not show optical isomerism.



ii. [Pt(en)Br<sub>2</sub>Cl<sub>2</sub>]: This complex is an octahedral complex of  $[M(AA)a_2b_2]$  type and has cis and trans, i.e. two geometrical isomers possible. cis-isomer is optically active, and gives two optically active isomers (d- and l-forms) whereas trans form is optically inactive. Thus there are three isomers.



**OIA** 



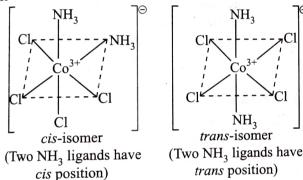


How many geometrical isomers are there for:

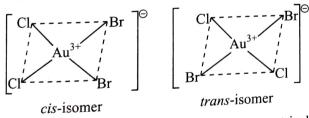
[AuCl<sub>2</sub>Br<sub>2</sub>]<sup>⊕</sup> (square planar)

$$[CuCl_2Br_2]^{2-}$$
 (tetrahedral)

Since  $[Co(NH_3)_2Cl_4]^{\Theta}$  is a  $[Ma_2b_4]$  type octahedral complex ion, it has two geometrical isomers which are cis and trans as shown below:



b. Since  $[AuCl_2Br_2]^{\Theta}$  ion is a  $[Ma_2b_2]$  type square planar complex ion, it has two geometrical isomers viz. cis and trans isomers.

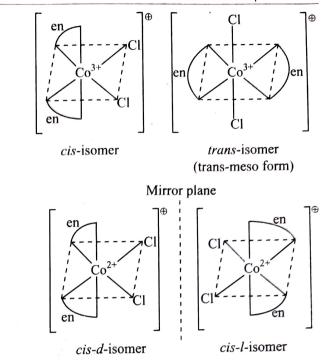


c.  $[CuCl_2Br_2]^{2-}$  is tetrahedral and hence has no geometrical isomer.

# EXAMPLE 7.6

A complex of the type  $[M(AA)_2X_2]$  is known to the optically active. What does this indicate about the structure of the complex? Give one example of such complex.

In  $[M(AA)_2X_2]$  since AA is a bidentate (symmetrical) ligand and X is a monodentate ligand, CN of M (central metal atom) is 6 and hence  $[M(AA)_2X_2]$  has octahedral geometry.  $[Co(en)_2Cl_2]^{\oplus}$ On is an example of the above type complex. This ion has cis and Tans isomers (geometrical isomers). Since cis-isomer is optically ctive, it has d- and l-isomers. Since trans-isomer is symmetrical 18 optically inactive and hence trans is meso form.



## EXAMPLE 7.7

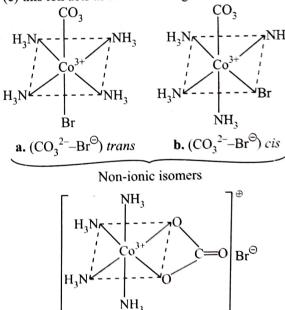
methods:

The formula Co(NH<sub>3</sub>)<sub>4</sub> CO<sub>3</sub>Br represents three isomers.

- i. Draw their structures
- How would you distinguish these isomers?

### Sol.

i. The structures of the three isomers represented by the given formula are given in the figure. In isomers (a) and (b). CO<sub>3</sub><sup>2-</sup> ion acts as a monodentate ligand but in isomer (c) this ion acts as a bidentate ligand.



- ii. These isomers can be distinguished by the following
  - a. Chemical method: When isomer (c) is treated with AgNO3 solution, yellow ppt. of AgBr is obtained.

c. Ionic isomer

b. Infra-red spectroscopic method: The absorption spectra of isomers (a) and (b) are different from that of isomer (c), since in (a) and (b), CO<sub>3</sub><sup>2-</sup> ion acts as a monodentate ligand but in (c) this ion acts as a bidentate ligands.

### EXAMPLE 7.8

On the basis of VBT, answer the following questions for the 4-coordinated complex compounds

- **a.**  $[CoBr_4]^{2-}$
- **b.**  $[Zn(CN)_4]^{2-}$
- c.  $[MnCl_4]^{2-}$
- i. What is the oxidation state of the central metal atom/ion?
- ii. What type of hybridisation is involved?
- iii. What is the geometry and magnetic behaviour of the complex ion/ compound?
- iv. Calculate the value of  $\mu_{\rm spin}$  only.

### Sol.

# a. [CoBr<sub>4</sub>]<sup>2-</sup>:

i. Let the oxidation state of Co in  $[CoBr_4]^{2-}$  be x.

Then, 
$$x + (-1) \times 4 = -2$$

x = -2 + 4 = +2

Therefore, oxidation state of Co in [CoBr<sub>4</sub>]<sup>2-</sup> is 2+.

ii. Co atom  $(3d^7 4s^2)$   $Co^{2^+} \text{ ion } (3d^7 4s^0)$   $Sp^3 \text{ hybridisation}$ 

 $\mathrm{Br}^{\Theta}$  is a weak ligand, so no pairing of 3d electrons occurs.

iii. Since Co<sup>2+</sup> ion in [CoBr<sub>4</sub>]<sup>2-</sup> shows sp<sup>3</sup> hybridisation, geometry of complex ion is tetrahedral, further as evident three unpaired electrons are present, so the complex ion is paramagnetic.

iv. 
$$\mu_{\text{spin}} = \sqrt{n(n+2)} \text{ BM}$$
  
 $\mu_{\text{spin}} \text{ only } = \sqrt{3(3+2)} = \sqrt{15}$   
 $= 3.87 \text{ BM}$  (:  $n = 3$ )

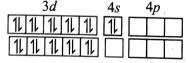
# b. [Zn(CN)<sub>4</sub>]<sup>2-</sup> ion:

i. Let oxidation state of Zn in  $[Zn(CN)_4]^{2-}$  be x

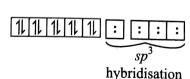
$$x + (-1) \times 4 = -2$$

$$x = +2$$

ii. Zn atom  $(3d^{10} 4s^2)$ Zn<sup>2+</sup> ion  $(3d^{10} 4s^0)$ 



 $\begin{bmatrix} Zn^{2+} & ion \\ (3d^{10} & 4s^{0}) \\ in & [Zn(CN)_{4}]^{2-} \end{bmatrix}$ 



iii. As evident,  $Zn^{2+}$  ion in  $[Zn(CN)_4]^{2-}$  is  $sp^3$  hybridised, with no unpaired electrons, therefore geometry of  $[Zn(CN)_4]^{2-}$  is tetrahedral and it is diamagnetic.

iv. 
$$\mu_{\text{spin}}$$
 only =  $\sqrt{n(n+2)}$  BM  
 $n = 0$ , =  $\mu_{\text{spin}}$  only = 0

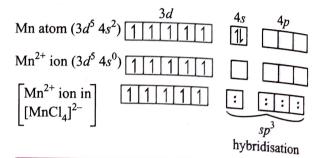
# c. [MnCl<sub>4</sub>]<sup>2-</sup>:

i. Let, oxidation state of Mn in  $[MnCl_4]^{2-}$  be x

$$x + (-1) \times 4 = -2$$
$$x = +2$$

Therefore, oxidation state of Mn in [MnCl<sub>4</sub>]<sup>2-</sup> is +2.

ii. Electronic configuration of



 $Cl^{\Theta}$  is a weak ligand, so no pairing of 3d electrons occurs.

- iii. Since  $Mn^{2+}$  ion is  $sp^3$  hybridised in  $[MnCl_4]^{2-}$ , geometry of  $[MnCl_4]^{2-}$  is tetrahedral. Magnetic behaviour of  $[MnCl_4]^{2-}$  is paramagnetic (n = 5).
- iv.  $\mu_{\text{spin}}$  only =  $\sqrt{5(5+2)}$  BM =  $\sqrt{35}$  BM = 5.91 BM

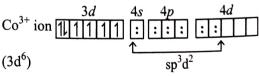
### EXAMPLE 7.9

- a. Explain why a knowledge of magnetic susceptibility of a complex is often necessary for a correct assignment of the electronic configuration according to valence bond theory.
- b. Draw valence bond representations of the electronic structures of (i) [CoF<sub>6</sub>]<sup>3-</sup> (paramagnetic) and (ii) [Co(CN)<sub>6</sub>]<sup>3-</sup> (diamagnetic)

### Sol.

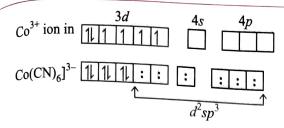
- a. Inner orbital complexes in which inner orbitals are involved i.e., d<sup>2</sup>sp<sup>3</sup> or dsp<sup>2</sup> or dsp<sup>3</sup>, electron pairing is necessary in some cases. The change in magnetic susceptibility moment is an indication of what orbitals are being used.
- **b. i.** Valence bond representation of  $[CoF_6]^{3-}$  (paramagnetic Co is  $Co^{3+}$  ion in  $[CoF_6]^{3-}$ ,

$$[\text{Co}(Z=27) \Rightarrow 3d^7 4s^2; \text{Co}^{3+} \Rightarrow 3d^6]$$



Since  $[CoF_6]^{3-}$  is paramagnetic, electron pairing will not take place and  $Co^{3+}$  ion will be  $sp^3d^2$  hybridised forming outer orbital complex.

- ii. Valence bond representation of  $[Co(CN)_6]^{3-}$  (diamagnetic).
  - In  $[Co(CN)_6]^{3-}$ , Co is present as  $Co^{3+}$



Since the complex ion is diamagnetic pairing of electrons takes place, resulting in Co<sup>3+</sup> ion in [Co(CN)<sub>6</sub>]<sup>3-</sup> complex ion to be d<sup>2</sup>sp<sup>3</sup> hybridised and hence forms inner orbital complex.

# EXAMPLE 7.10

Magnetic moment of [CoI<sub>4</sub>]<sup>2-</sup> is 3.8 BM. Using valence bond approach, predict the structure of [CoI<sub>4</sub>]<sup>2</sup>-.

 $\mu_s = 3.80$  BM corresponds to n = 3.

Number of unpaired electrons = 3

Coordination number (CN) and oxidation state (OS) of Co in the complex are 4 and +2 respectively.

$$\operatorname{Co}(Z=27) \Rightarrow 3d^{7}4s^{2}, \operatorname{Co}^{2+} \Rightarrow 3d^{7}$$

$$\operatorname{Co}^{2+} \operatorname{ion}(3d^{7}) \quad \boxed{1 \quad 1 \quad 1 \quad 1 \quad 1} \quad \boxed{ } \quad \boxed{ } \quad \boxed{ } \quad \operatorname{Co}^{2+} \operatorname{ion} \operatorname{in}$$

$$[\operatorname{CoI}_{4}]^{2-} \operatorname{ion} \quad \boxed{ } \quad \underbrace{ 1 \quad 1 \quad 1 \quad 1 \quad 1} \quad \boxed{ } \quad \underbrace{ \dots \dots \dots}$$

$$sp^{3} \operatorname{hybridisation}$$

Since the complex is paramagnetic with n = 3, electron pairing not take place and Co<sup>2+</sup> ion in the complex is tetrahedral.

## EXAMPLE 7.11

i. A complex of a certain metal ion has a magnetic moment of 4.90 BM Another complex of the same metal ion in the same oxidation state has a zero magnetic moment. The central metal ion could be which of the following?

- b. Mn<sup>3+</sup>
- c. Fe<sup>2+</sup>
- ii. Refer to the question above, if a metal ion has complex ion and with magnetic moments 4.90 and 2.8 BM which one of these is the central metal ion.

a. Cr3+

- b. Mn<sup>3+</sup>
- c  $Fe^{2+}$  d  $Co^{2+}$

i. c.  $\mu = 4.90$  B.M. corresponds to n = 4 which corresponds  $d^0$ configuration. In a weak field ligands, d<sup>6</sup> configuration will have 4 unpaired electrons. In strong field ligands, d<sup>6</sup> configuration will have no unpaired electrons with zero magnetic moment value.

Fe<sup>2+</sup> have 3d<sup>6</sup> configuration.

In weak field ligands:

$$\frac{1}{\text{Fe}^{2+}} \frac{1}{(a^6)} \text{ ion} \qquad \frac{1}{n = 4 \text{ (CFT)}} e_g^2$$

In strong field ligands:

$$\frac{1 + 1 + 1}{\text{Fe}^{2+}(d^6) \text{ ion}} \quad \dots \quad ---- e_g^0$$

$$n = 0 \text{ (VBT)} \qquad n = 0 \text{ (CFT)}$$

ii. b.  $\mu = 4.9$  BM corresponds to n = 4 and for  $\mu = 2.80$  BM corresponds to n = 2.

For  $d^4$  configuration, in a weak field ligands it will have 4 unpaired electrons. In strong field ligand,  $d^4$ configuration will have one paired electrons and two unpaired electrons.

Note:  $d^1$  to  $d^3$  configuration, no pairing will occur whether the ligand field is weak or strong. But for  $d^4$  configuration only one pairing will occur in strong field ligands

Therefore,  $Mn^{3+}$  have  $3d^4$  configuration.

In weak field ligands:

$$\frac{1}{Mn^{3+}} \frac{1}{(d^4) \text{ ion}} \dots \frac{1}{1} \frac{1}{t_{2g}^3}$$

$$n = 4 \text{ (VBT)} \qquad n = 4 \text{ (CFT)}$$

In strong field ligands:

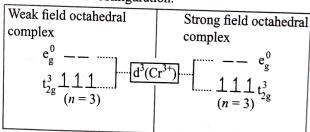
$$\frac{1}{Mn^{3+}} \frac{1}{(d^4) \text{ ion}} \qquad --- e_g^0$$

$$n = 2 \text{ (VBT)} \qquad n = 2 \text{ (CFT)}$$

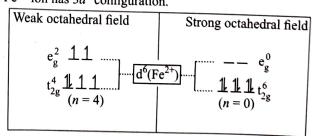
## EXAMPLE 7.12

Find out the number of unpaired electrons in strong and weak octahedral field for Cr3+ and Fe2+ ions.

Sol. Cr<sup>3+</sup> ion has 3d<sup>3</sup> configuration.



Number of unpaired electrons, n = 3 (in both cases)  $Fe^{2+}$  ion has  $3d^6$  configuration.



Number of unpaired electrons; n = 4, in weak octahedral field, n = 0, in strong octahedral field.

### EXAMPLE 7.13

Distinguish between the possibilities in complex ions of  $\Delta = 0$ and CFSE = 0. Give an example of each.

Soil  $\Delta = 0$  means no crystal field splitting i.e. case of free gaseous ion.

CFSE = 0 means equal occupancy of all the *d*-orbitals, i.e.  $d^5$  weak field ion, and  $d^{10}$  both weak and strong field ion.

Example of case when  $\Delta_0 = 0$ ,  $Zn^{2+}$  gaseous ion. CFSE = 0 in  $[Mn(H_2O)_6]^{2+}$  and  $[Zn(H_2O)_6]^{2+}$ 

### EXAMPLE 7.14

Determine the crystal field stabilisation energy of a  $d^6$  complex having  $\Delta_0 = 25000 \text{ cm}^{-1}$  and  $P = 15000 \text{ cm}^{-1}$ .

Sol. For 
$$d^6$$
 complex, when  $\Delta_0 = 25000 \text{ cm}^{-1}$  and  $P = 15000 \text{ cm}^{-1}$ , i.e.  $\Delta_0 > P$ .

1 1 1 1 1 1 .....  $e_g^0$  ..... 1 1 1 1  $e_g^0$ 

CFSE = 
$$-(0.4 \times 6) \Delta_0 + 3P$$
  
=  $-(0.4 \times 6) \times 25000 \text{ cm}^{-1} + 3 \times 15000 \text{ cm}^{-1}$   
=  $-15000 \text{ cm}^{-1}$ 

### EXAMPLE 7.15

On the basis of CFT, predict the geometry of the compound,  $K_3[Mn(CN)_6]$ . Also calculate the value of  $\mu_{spin}$  only of the compound.

Sol. In  $K_3[Mn(CN)_6]$ ,  $[Mn(CN)_6]^{3-}$  is the complex ion. In  $[Mn(CN)_6]^{3-}$  the oxidation state of central metal ion, i.e. Mn is +3.  $(Mn = 3d^5 4s^2, Mn^{3+} = 3d^4)$ .

CN of Mn in  $[Mn(CN)_6]^{3-}$  is 6, hence it is an octahedral complex.  $CN^{\Theta}$  ion is a strong field ligands, therefore  $[Mn(CN)_6]^{3-}$  is low spin octahedral complex and hence  $Mn^{3+}$  ion (in  $[Mn(CN)_6]^{3-}$ ) is  $t_{2g}^{4} e_{g}^{0}$ .

Splitting of *d*-orbitals in octahedral geometry with n = 2

$$\mu_{\rm spin} = \sqrt{2(2+2)} = 2.83 \text{ BM}$$

### EXAMPLE 7.16

The enthalpy of hydration of the  $Fe^{2^+}$  iion is 11.4 kcal/mol higher than would be expected if there were no crystal field stabilisation energy. Assuming the equo complex to be high spin, estimate the magnitude of  $\Delta_0$  for  $[Fe(H_2O)_6]^{2^+}$  ion.

Sol. Fe<sup>2+</sup> is t<sub>2g</sub><sup>4</sup> e<sub>g</sub><sup>2</sup> in weak field environment

$$\begin{array}{rcl}
11 & e_g^2 \\
11 & 1 & 1 & t_{2g}^4 \\
\text{CFSE} & = -(0.4 \times 4) \Delta_0 + (0.6) \times 2) \Delta_0 \\
& = -1.6 \Delta_0 + 1.2 \Delta_0 \\
& = -0.4 \Delta_0
\end{array}$$

 $\Delta H_{hyd}$  is higher because the energy of the complex is lowered by  $-11.4\ kcal/mol.$ 

CFSE = 
$$-11.4 \text{ kcal/mol} = -0.4 \Delta_0$$
  
 $\Delta_0 = \frac{-11.4}{0.4} = -28.5 \text{ kcal / mol}$ 

## EXAMPLE 7.17

If a complexing metal of the first transition series has a di configuration for what values of 'i' could magnetic properties alone distinguish between strong field and weak field ligands in octanderal coordination?

**Sol.** When i = 4, 5, 6 and 7, i.e.  $d^4$ ,  $d^5$ ,  $d^6$  and  $d^7$  configuration, magnetic values alone can distinguish between strong field and weak field ligands in octahedral coordination.

### EXAMPLE 7.18

In terms of CFT, explain why a  $d^9$  octahedral complex with six identical ligands is not expected tom have all size M-L distances identical.

**Sol.** For  $d^9$  octahedral complex, the cofiguration will be  $t_{2g}^6 e_{g}^3$ 

$$\frac{1}{d_{x^{2}-y^{2}}} \frac{1}{d_{z^{2}}} e_{g}^{3}$$

$$\frac{1}{d_{xy}} \frac{1}{d_{yz}} \frac{1}{d_{xz}} t_{2g}^{6}$$

One of the e<sub>g</sub> orbitals is completely filled and other is half filled and hence interaction with the ligands is expected to be different.

### EXAMPLE 7.19

Derive the geometry of the complex compound corresponding to the brown ring in nitrate test. Predict the magnetic moment of the complex.

**Sol.** Brown ring formed in the nitrate test is due to the formation of the complex ion  $[Fe(H_2O)_5(NO)]^{2+}$  in which Fe and NO both are present as  $Fe^{\oplus}$  and  $NO^{\oplus}$  (nitrosonium) ions respectively.  $Fe^{\oplus}$  ion acts as the central metal ion and  $NO^{\oplus}$  ion acts as a ligand. Five  $H_2O$  molecules also act as ligands.

Since CN of Fe<sup> $\oplus$ </sup> ion is 5 + 1 = 6,  $[\text{Fe}(\text{H}_2\text{O})_5(\text{NO})]^{2+}$  is an octahedral complex ion which is formed by  $sp^3d^2$  hybridisation and has 3 unpaired electrons (i.e. n = 3).

Thus  $[Fe(H_2O)_s(NO)]^{2+}$  ion is paramagnetic and its

$$\mu = \sqrt{3 \times (3+2)}$$
 BM =  $\sqrt{15}$  = 3.89 BM

	Fe (Z = 26)	$3d^6 4s^2$			
a. b.	$\text{Fe}^{\oplus}$ ion is the complex $(3d^6 4s^1)$	$3d^6$	4s <sup>1</sup>	$4p^0$	$4d^0$
μ.		11111	1		
c.	NO <sup>®</sup> is a strong field ligand so pairing	3d <sup>7</sup>	$4s^0$	$4p^0$	$4d^0$
	of only 1 electron occurs. H <sub>2</sub> O is a	11111	_		
	weak field ligand, so pairing does not occur with five H <sub>2</sub> O ligands				
		2.17	45	4 <i>p</i>	4 <i>d</i>
d.	$[Fe^{\oplus}(H_2O)_5NO^{\oplus}]$	3d <sup>7</sup>	45	<b>-</b> p	ти 
		$\frac{1}{(n=3)}$		<u></u>	·· ··
		(n-3)	NO <sup>⊕</sup>	$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	O O H, H,
				$\Pi_2$ $\Pi_2$ $\Pi_2$	112 112
				1	
				ybridisation, or	
			(	octahedral geon	netry

# AMPLE 7.20

Which of the electronic configuration according to crystal field theory of the compound is correct [MnF<sub>6</sub>]<sup>4-</sup>?

a. 
$$3(t_{2g}^5 e_g^0)$$

b. 
$$3(t_{2g}^3 e_g^2)$$

c. 
$$4(e_g^2 t_{2g}^3)$$

d. 
$$4(t_{2g}^3 e_g^2)$$

Which of the electronic configuration according to crystal field theory of the compound Rh<sup>+2</sup> with CN = 6 is correct when  $\Delta > P$ ?

a. 
$$3(t_{2g}^6 e_g^1)$$

b. 
$$4(t_{2g}^6 e_g^1)$$

c. 
$$3(t_{2g}^5 e_g^1)$$

d. 
$$4(t_{2g}^5 e_g^2)$$

According to crystal field theory, the electronic configuration of the  $[Cr(H_2O)_6]^{2+}$  ion, when  $(\Delta < P)$  $(\Delta = CFSE, P = Pairing energy).$ 

a. 
$$3(t_{2g}^3 e_g^1)$$

b. 
$$4(t_{2g}^{3} e_{g}^{1})$$

c. 
$$3(e_g^1 t_{2g}^1)$$

d. 
$$3(e_g^3 t_{2g}^1)$$

- According to crystal field theory, the electronic configuration of the [FeCl<sub>4</sub>] ion is
- a.  $3(t_2^3 e^2)$
- b.  $3(e^2 t_2^3)$
- c.  $4(t_2^3 e^2)$
- d.  $4(e^2 t_2^3)$
- According to crystal field theory, the electronic configuration of the compound  $[Mn(CN)_4]^{2-}$  is  $(\Delta > P)$ :
- a.  $4(e^4 t_2^1)$
- b.  $3(e^2 t_2^3)$
- c.  $4(e^2 t_2^3)$
- d.  $3(e^4 t_2^1)$
- Crystal field splitting energy (CFSE) for the complex  $[Cr(H_2O)_6]^{2+}$  is when  $(\Delta < P)$
- a.  $-1.2 \Delta_0$
- b.  $-0.6 \, \Delta_0$
- d.  $1.2 \, \Delta_0$
- Crystal field splitting energy (CFSE) for the complex
- $[\operatorname{Cr}(\operatorname{NH}_3)_6]^{2+}$  is (when  $\Delta > P$ ) a.  $-1.6 \Delta_0 + P$ 
  - b.  $1.6 \Delta_0 + P$
- c.  $-2.4 \Delta_0 + P$
- d.  $2.4 \Delta_0 + P$

8. Crystal field splitting energy (CFSE) for the complex  $[Cr(H_2O)_6]^{2+}$  is when  $P = 20925 \text{ cm}^{-1}$  and

$$\Delta_0 = 10462.5 \text{ cm}^{-1} \text{ (1 kJ mol}^{-1} = 83.7 \text{ cm}^{-1})$$

- a. -75 kJ mol<sup>-1</sup>
- b. 75 kJ mol<sup>-1</sup>
- c. 750 kJ mol<sup>-1</sup>
- d. -750 kJ mol<sup>-1</sup>
- 9. Crystal field splitting energy (CFSE) for the complex  $[Cr(NH_3)_6]^{2+}$  is when P = 125 and  $\Delta_0 = 250$  kJ mol<sup>-1</sup>
  - a. 525 kJ mol<sup>-1</sup>
- b. 275 kJ mol<sup>-1</sup>
- c.  $-275 \text{ kJ mol}^{-1}$
- d. -525 kJ mol<sup>-1</sup>
- 10. In which structure crystal field splitting energy (CFSE) for octahedral complex will be zero when  $\Delta < P$ .
  - a.  $d^5$

b. d6

- c.  $d^8$
- d. d9
- 11. In which structure crystal field splitting energy (CFSE) for octahedral complex will be minimum or zero when  $\Delta > P$ .
  - a.  $d^5$

b. d6

- $d. d^{10}$
- 12. Crystal field splitting energy (CFSE) for the complex [FeCl<sub>4</sub>]  $\Theta$  is when  $\Delta \leq P$ .
  - a.  $-1.0 \Delta_t$
- b. 1.0 Δ,

c. 0

- d. -1.8 Δ,
- 13. Crystal field splitting energy (CFSE) for the complex  $[Fe(CN)_4]^{\Theta}$  is when  $\Delta > P$ .
  - a. -2.0
- b.  $\Delta + P$
- c. 2+P
- d. 0
- 14. Crystal field splitting energy (CFSE) for the complex  $[\text{FeO}_4]^{2-}$  is when  $\Delta = 125$  and  $P = 250 \text{ kJ mol}^{-1}$ .
  - a.  $-1.2 \Delta_t$
- b. 1.2 Δ,
- c. -8
- d. 8
- 15. CFSE for  $d^6$  octahedral complex having  $\Delta = 250$  and  $P = 125 \text{ kJ mol}^{-1} \text{ is}$ 
  - a. 350 kJ mol<sup>-1</sup>
- b.  $-350 \text{ kJ mol}^{-1}$
- c. 475 kJ mol<sup>-1</sup>
- d. -475 kJ mol<sup>-1</sup>

- 16. The enthalpy of hydration of  $Cr^{+2}$  is -460 kcal mol<sup>-1</sup>. In the absence of CFSE, the value for  $\Delta H = -424$  kcal mol<sup>-1</sup>. What is the value of  $\Delta_0$  for  $[Cr(H_2O)_6]^{2+}$ 
  - a. 60 kcal mole<sup>-1</sup>
- b. 60 kcal mole<sup>-1</sup>
- c. 25.7 kcal mole<sup>-1</sup>
- d. -25.7 kcal mole<sup>-1</sup>

### Sol.

**Note:** Pairing energy should be considered only for low spin complexes (strong ligand) because electron foresfully paired so pairing energy is required. But for high spin complexes (weak ligand), pairing energy is not considered because  $e^{-}$ 's pairs in natural way as like free metal ion.

- 1. b. Octahedral complex, CN = 6Weak ligand  $(F^{\odot})$   $Mn = 3d^5 4s^2$ ,  $Mn^2 = 3d^5$  $\therefore 3(t_{2g}^3 e_g^2)$
- 2. **b.** Rh =  $4d^7 5s^2$  Rh<sup>+2</sup> =  $4d^7$ When  $\Delta > P$  (Strong field and pairing occurs) Structure =  $4(t_{2g}^6 e_g^1)$
- 3. a. Octahedral complex, when  $(\Delta < P)$  (weak field) (high spin state) (No pairing)  $Cr = 3d^5 4s^1$ ,  $Cr^{+2} = 3d^4$   $\therefore$  Structure =  $3(t_{2\sigma}^3 e_g^1)$
- **4. b.** Tetrahedral complex, CN = 4. Weak ligand  $(Cl^{\Theta})$  (No pairing; High spin complex)  $Fe = 3d^6 4s^2$ ,  $Fe^{+3} = 3d^5$   $\therefore$  Structure =  $3(e^2 t_2^3)$
- 5. b. Tetrahedral complex, CN = 4
   Mn = 3d<sup>5</sup>4s<sup>2</sup>, Mn<sup>+2</sup> = 3d<sup>5</sup>, Δ > P
   (Strong field but pairing does not take place, in tetrahedral complexes)
   ∴ Structure = 3(e<sup>2</sup> t<sup>3</sup><sub>2</sub>)
- 6. b. Octahedral complex, CN = 6,  $\Delta < P$ (Weak ligand, no pairing, high spin state)  $Cr = 3d^5 4s^1$ ,  $Cr^{+2} = 3d^4$  Structure =  $(t_{2g}^3 e_g^1)$  $CFSE = (-0.4 \times 3 + 0.6) \Delta_0 = -0.6\Delta_0$
- 7. a. Octahedral complex, CN = 6,  $\Delta > P$ (Strong ligand, one pairing, low spin state)  $Cr = 3d^5 4s^1$ ,  $Cr^{+2} = 3d^4$  Structure is  $3(t^4_{2g} e_g^0)$  $CFSE = (-0.4 \times 4) \Delta_0 + P = -1.6\Delta_0 + P$
- 8. a.  $\Delta < P$  (weak field, no pairing, high spin state) Octahedral complex, CN = 6  $Cr = 3d^5 4s^1$ ,  $Cr^{+2} = 3d^4$  Structure is:  $3(t_{2g}^3 e_g^1)$   $P = \frac{20925 \text{ cm}^{-1}}{83.7} = 250 \text{ kJ mol}^{-1}$  $\Delta_0 = \frac{10462.5 \text{ cm}^{-1}}{83.7} = 125 \text{ kJ mole}^{-1}$ .

CFSE = 
$$(-0.4 \times 3 + 0.6) \Delta_0 = -0.6\Delta_0 = -0.6 \times 125$$
  
=  $-75 \text{ kJ mol}^{-1}$ 

- 9. c.  $\Delta > P$ , strong field, pairing, low spin

  Octahedral complex, CN = 6  $Cr = 3d^54s^1$ ,  $Cr^{+2} = 3d^4$  Structure is  $3(t_{2g}^4 e_g^0)$   $CFSE = (-0.4 \times 4) \Delta_0 + P = -1.6 \times 250 + 125$   $= -275 \text{ kJ mol}^{-1}$
- 10. a.  $\Delta < P$ , weak field, no pairing, octahedral. Structure of  $d^5 = (t_{2g}^3 e_g^2) = -0.4 \times 3 + 2 \times 0.6 = 0$
- 11. d. If  $\Delta < P$ , weak field, no pairing  $d^5 = t_{2g}^3 e_g^2$ CFSE =  $-0.4 \times 3 + 2 \times 1.6 = 0$ If  $\Delta > P$ , strong field, pairing  $d^5 = t_{2g}^5 e_g^0$ CFSE =  $-0.4 \times 5 = -2\Delta$ For  $d^{10}$ ,  $\Rightarrow t_{2g}^6 e_g^4 = -0.4 \times 6 + 0.6 \times 4 = 0$
- 12. c. Tetrahedral complex, CN = 4( $\Delta < P$  weak ligand, no pairing, high spin).  $Fe = 3d^6 4s^2$ ,  $Fe^{+3} = 3d^5$  Structure is  $(e^2 t_2^3)$  $CFSE = -0.6 \times 2 + 0.4 \times 3 = 0$
- 13. d. Tetrahedral complex, CN = 4,  $\Delta > P$ Strong ligand, but pairing does not take place in tetrahedral complexes.

Fe = 
$$3d^6 4s^2$$
 Fe<sup>+3</sup> =  $3d^5 \Rightarrow (e^2 t_2^3)$   
CFSE =  $(-0.6 \times 2 + 0.4 \times 3) \Delta_t = 0.0$ 

- 14. a. Tetrahedral complex, CN = 4,  $\Delta < P$ Weak ligand, no pairing, high spin  $Fe = 3d^64s^2$ ,  $Fe^{+6} = 3d^2 \Rightarrow (e^2 t_2^0)$  $CFSE = (-0.6 \times 2)\Delta_t = -1.2\Delta_t$
- **15. b.** Octahedral complex,  $\Delta > P$  strong field, pairing, low spin. Structure is  $(t_{2g}^6 e_g^0)$

If weak ligand 
$$(t_{2g}^{\phantom{2g}4} e_{g}^{\phantom{2g}2})$$
 111

If strong ligand  $(t_{2g}^{\phantom{2g}6} e_{g}^{\phantom{2g}0})$  1111

It means pairing energy is required for 2 electrons, since one pairing is already done in weak ligand CFSE =  $(-0.4 \times 6) \Delta_0 + 2P = -2.4 \times 250 + 2 \times 125$ =  $-600 + 250 = -350 \text{ kJ mole}^{-1}$ 

16. a.  $Cr = 3d^54s^1$ ,  $Cr^{+2} = 3d^4$ . Structure is  $(t_{2g}^3 e_g^1)$   $CFSE(-0.4 \times 3 + 0.6) \Delta_0 = -0.6 \Delta_0$ .  $-0.6 \Delta_0 = (-460) - (-424) = -36 \text{ k cal mol}^{-1}$   $\Delta_0 = \frac{-36}{-0.6} = 60 \text{ kcal mol}^{-1}$  $= 60 \times 350 \text{ cm}^{-1} = 21000 \text{ cm}^{-1}$ 

$$= 60 \times 350 \text{ cm}^{-1} = 21000 \text{ cm}^{-1}$$

$$(1 \text{ kcal mol}^{-1} = 350 \text{ cm}^{-1})$$

# ingle Correct Answer Type Terminology and Ligands Select the correct IUPAC name for $\int_{1}^{1} (\pi - C_5 H_5)_2 (\sigma - C_5 H_5)_2$ ]:

bis (\(\eta^5\)-cyclopentadiene) bis (cyclopentadiene) titanate(IV)

η) bis (η<sup>5</sup>-cyclopentadienyl) bis (cyclopentadienyl)

(β) bis (cyclopentadienyl) bis (η<sup>5</sup>- cyclopentadienyl) titanate(IV)

... (μ) bis (η<sup>5</sup>-cyclopentadiene) bis (cyclopentadiene)

, Select the correct IUPAC name for  $[Mo(\sigma-C_3H_5) (\pi-C_5H_5) (CO_3)]$ 

(I) Tricarbonyl (η<sup>5</sup>-cyclopentadienyl) allyl molybdate(II)

(2) Allytricarbonyl (η<sup>5</sup>-cyclopentadiene) molybdate(II)

(3) Allyltricarbonyl (η<sup>5</sup>-cyclopentadienyl) molybdenum(II)

(4) Allyl tricarbonyl (η<sup>5</sup>-cyclopentadienyl) molybdenum(II)

1 JUPAC name for  $[Fe(CO)_2(\sigma-C_5H_5)(\pi-C_5H_5)]$  complex:

(1) Dicarbonyl (η<sup>5</sup>-cyclopentadienyl) (cyclopentadienyl) ferrate(II)

(2) Dicarbonyl (η<sup>5</sup>-cyclopentadiene) (cyclopentadienyl)

(3) Dicarbonyl (η<sup>5</sup>-cyclopentadienyl) (cyclopentadienyl)

(4) Dicarbonyl ( $\eta^5$ -cyclopentadienyl) ( $\eta^5$ -cyclopentadienyl) iron(II)

Select the correct IUPAC name for  $[Cr(C_6H_6)(CO)_3]$ :

(1) ( $\eta^6$ -benzene) tricarbonylchromate(0)

(2) Tricarbonyl ( $\eta^6$ -benzene)chromate(0)

(3) Tricarbonyl ( $\eta^6$ -benzene)chromium(0)

(4) (n<sup>6</sup>-benzene) tricarbonylchromium(0)

IUPAC name for complex  $[Mn(\pi-C_6H_5)(CO)_3]$ :

(1) Tricarbonyl (η<sup>5</sup>-cyclopentadiene)manganese(I)

(2) Tricarbonyl ( $\eta^5$ -cyclopentadiene)manganate(I)

(3) Tricarbonyl (η<sup>5</sup>-cyclopentadienyl)manganese(I)

4) (η<sup>5</sup>-cyclopentadienyl) tricarbonyl manganese(1)

Ligand with two or more points of attachment to single metal atoms are called:

l) Monodentate ligand

(2) Chelating ligand

3) Ambidentate ligand

(4) None of these

The number of ions produced by the complex

 $Cr(NH_3)_4Cl_2]ClO_3$  is

(2) 3

(4)6

hich of the following is a tridentate ligand?

NO,<sup>⊖</sup>

(2) Oxalate ion

) Glycinate ion

(4) Dien

9. Coordination number of calcium is six in:

(1)  $[Mg(EDTA)]^{2-}$ 

(2) MgC<sub>2</sub>O<sub>4</sub>

(3)  $[Mg(C_2O_4)_2]^{2-}$ 

d. MgSO<sub>4</sub>·4H<sub>2</sub>O

10. Coordination number of Cu<sup>2+</sup> in CuSO<sub>4</sub>·5H<sub>2</sub>O is

(1)5(3)3 (2)4(4)2

11. The closed ring compounds formed by bidentate ligands, on binding to a metal or metal ions are called:

(1) Monodentate

(2) Chelates

(3) Ambidentate

(4) None of these

12. Which is the pair of ambidentate ligand?

 $(1) \text{ CN}^{\Theta}, \text{NO}_2^{\Theta}$ 

 $(2)NO_3^{\Theta}$ , SCN $^{\Theta}$ 

 $(3) N_3^{\Theta}, NO_2^{\Theta}$ 

 $(4) \text{NCS}^{\ominus}, C_2 O_4^{2-}$ 

13. Number of water molecules acting as ligands in CuSO<sub>4</sub>·5H<sub>2</sub>O, ZnSO<sub>4</sub>·5H<sub>2</sub>O, FeSO<sub>4</sub>·7H<sub>2</sub>O respectively are

(1) 5, 5, 7

(2)4, 5, 4

(3) 4, 4, 6

14. Select the correct IUPAC name for

 $[Pt(C_5H_5N)_4]$   $[PtCl_4]$  complex:

(1) Tetrapyridineplatinate(II) tetrachloridoplatinate(II)

(2) Tetrapyridineplatinate(II) tetrachloridoplatinate(II)

(3) Tetrapyridineplatinate(II) tetrachloridoplatinum(II)

(4) Tetrapyridineplatinum(II) tetrachloridoplatinate(II)

15. Select the correct IUPAC name for  $[C_4H_4Fe(CO)_3]$  complex:

(1)  $\eta^4$ -cyclebutadiene tricarbonyliron(0)

(2) Tricarbonyl ( $\eta^4$ -cyclobutadienyl) iron(0)

(3) Tricarbonyl ( $\eta^4$ -cyclobutadiene) iron(1)

(4) Tricarbonyl ( $\eta^4$ -cyclobutadiene) iron(0)

16. Oxidation state of "V" in Rb<sub>4</sub>K[HV<sub>10</sub>O<sub>28</sub>] is

(1) + 5

(2)+6

 $(3) + \frac{7}{5}$ 

(4)+4

17. Coordination number of Cr is six. A complex with  $C_2O_4^{2-}$ , en and superoxide  $O_2^{\Theta}$  will be in the ratio to make complex  $[\operatorname{Cr}(\operatorname{C}_2\operatorname{O}_4)_{\mathfrak{x}}, (\operatorname{en})_{\mathfrak{y}} (\operatorname{O}_2)_{\mathfrak{z}}]^{\Theta}$ 

(1) 1

(2) 1 2

(3) 1 (4) 21

18. The compound  $[CoCl_3I(C_5H_5N)_2]$ Br will show the chemical test for which of the following ions?

 $(1) \operatorname{Br}^{\Theta}$ 

(3) I<sup>⊖</sup>

(4) Br<sup>⊖</sup> as well as Cl<sup>⊖</sup>

19. The correct IUPAC name of [Mn<sub>3</sub>(CO)<sub>12</sub>] is

(1) Dodecacarbonylmanganate(0)

(2) Dodecacarbonylmanganic(II)

- (3) Dodecacarbonyltrimanganese(0)
- (4) Manganiododecarbonyl(0)
- 20. The correct name of

$$(CO)_3$$
Fe $CO$ Fe $(CO)_3$  is

- (1) Tri-μ-carbonylbis(tricarbonyl iron(0))
- (2) Hexacarbonyliron(III)µ-tricarbonylferrate(0)
- (3) Tricarbonyliron(0)µ-tricarbonyliron(0)
- (4) Nonacarbonyl iron
- 21. The correct IUPAC name of the complex:

$$H_3C$$
— $C$ = $N$  $\searrow$   $C$ 0 $C$  $I_2$  is  $H_3C$ — $C$ = $N$  $\nearrow$   $O$ H

- (1) Dichloridodimethylglyoximatocobalt(II)
- (2) Bis(dimethylglyoxime) dichlorocobalt(II)
- (3) Dimethylglyoximecobalt(II) chloride
- (4) Dichloridodimethylglyoxime-N,N-cobalt(II)
- 22. The correct IUPAC name of [AlCl<sub>3</sub>]·4(EtOH) is
  - (1) Aluminium(II) chloride-4-ethanol
  - (2) Trichloridoaluminium(III)-4-ethanol
  - (3) Aluminium(III) chloride-4-hydroxyethane
  - (4) Aluminium chloride-4-ethanol
- 23. In octaamine-μ-dihydroxodiiron(III) sulphate, the number of bridging ligands is
  - (1)2

(2) 1

(3) 3

- (4) None
- 24. The IUPAC name of the complex having formula  $[(CO)_{3}Fe(CO)_{3}Fe(CO)_{3}]$  is
  - (1) Monocarbonylferrate(0)
  - (2) Tricarbonyliron(0)-μ-tricarbonyliron(0)
  - (3) Tri-μ-carbonylbis-{tricarbonyliron(0)}
  - (4) Hexacarbonyl-μ-tricarbonyliron(III)
- 25. A group of atoms can function as a ligand only when
  - (1) It is a small molecule
  - (2) It is capable of acting as donor of electron pair
  - (3) It is a negatively charged ion
  - (4) It is a positively charged ion.
- 26. Which of the following is most likely structure of CrCl<sub>2</sub>·6H<sub>2</sub>O if 1/3 of total chlorine of the compound is precipitated by adding AgNO3 to its aqueous solution?
  - (1) CrCl<sub>3</sub>·6H<sub>2</sub>O
- (2) [Cr(H<sub>2</sub>O)<sub>3</sub>Cl<sub>3</sub>] (H<sub>2</sub>O)<sub>3</sub>
- (3)  $[CrCl_2(H_2O)_4]Cl.2H_2O$  (4)  $[CrCl\cdot(H_2O)_5]Cl_2\cdot H_2O$
- 27. The coordination number of the central ion may be obtained from
  - (1) The number of ionic bonds formed with the surrounding
  - (2) The number of coordinate bonds formed with the surrounding atoms
  - (3) The number of ions of opposite charge immediately surrounding the specific ion

- (4) None of the above
- 28. Which of the following is nonionisable?
  - (1)  $[Co(NH_3)_3Cl_3]$
- (2) [Co(NH<sub>3</sub>)<sub>4</sub>Cl<sub>2</sub>]Cl
- (3)  $[Co(NH_3)_5Cl]Cl_2$
- $(4) [Co(NH_3)_6]Cl_3$
- 29. Which of the following pair contains complex salt and double salt respectively?
  - (1)  $FeSO_4$ ,  $K_4[Fe(CN)_6]$
  - (2)  $[Cu(NH_3)_4]SO_4$ ,  $FeSO_4 \cdot 7H_2O$
  - (3)  $[Cu(NH_3)_4]SO_4$ ,  $K_2SO_4Al_2(SO_4)_3\cdot 24H_2O_4$
  - (4)  $MgSO_4$ ·7H<sub>2</sub>O,  $CuSO_4$ ·5H<sub>2</sub>O
- 30. In which of the following compounds the metal is in the lowest oxidation state?
  - (1)  $[Co(NH_3)_5Br]SO_4$
- (2)  $Fe_3[Fe(CN)_6]_2$
- (3)  $[Mn_2(CO)_{10}]$
- (4)  $K[PtCl_3(C_2H_4)]$
- 31. Which of the following can be termed as mixed complex?
  - (1)  $K_4[Fe(CN)_6]$
- (2)  $[Cu(NH_3)_4]SO_4$
- (3) [Co(NH<sub>3</sub>)<sub>4</sub>NO<sub>2</sub>Cl]Cl
- (4) K<sub>2</sub>FeSO<sub>4</sub>
- 32. The oxidation number of Co in  $[Co(en)_3]_2(SO_4)_3$  is
  - (1) + 2

(2) + 1

(3) + 3

- (4)+6
- 33. The IUPAC name for the coordination compound  $Na_3[Ag(S_2O_3)_2]$  is
  - (1) Sodium silverthiosulphate(I)
  - (2) Sodium silverhyposulphate(I)
  - (3) Sodium bis[argentothiosulphate(I)]
  - (4) Sodium bis(thiosulphato)argentite
- 34. The IUPAC name for the coordination compound  $[CuCl_2(CH_3NH_2)_2]$  is
  - (1) Dimethylamine copper(II) chloride
  - (2) Bis(dimethylamine copper(II) chloride
  - (3) Dichloridobis(methylamine) copper(II)
  - (4) Dichlorobis(dimethylamine) copper(II)
- **35.** The IUPAC name for  $[Al(OH)(H_2O)_5]^{2+}$  is
  - (1) Pentahyroaluminium hydroxide
  - (2) Aquometaaluminate ion
  - (3) Pentaaquaaluminate(III) hydroxide
  - (4) Pentaaquahydroxoaluminium(III)
- **36.** The IUPAC name for  $[Pt(Br)(Cl)(NH_3)_3(NO_2)]Cl$  is
  - $(1) \ Triammine chlorido bromidon itroplatinum (IV) \ chloride$
  - (2) Triamminebromidochloridonitroplatinum(IV) chloride
  - (3) Triamminnitrochlorobromoplatinum(IV) chloride
  - (4) Triamminechloronitrobromoplatinum(IV) chloride
- 37. The oxidartion number of Cr in  $[Cr(C_6H_6)_2]$  is
  - (1)0

(2) + 2

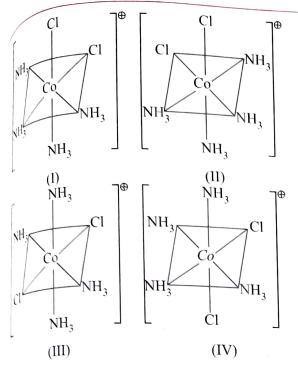
(3) + 3

- (4) + 6
- 38. Which of the following has five donor (coordinating) sites? (1) Ethylenediaminetriacetate ion

  - (2) Diethylene triamine
  - (3) Ethylenediaminetetracetate ion
  - (4) Triethylene tetramine.

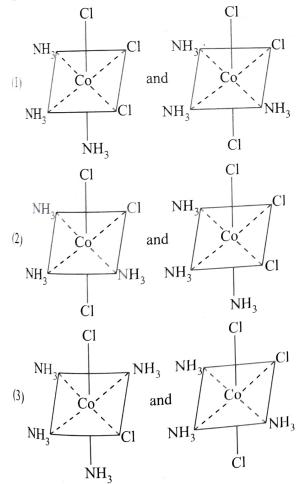
			Coordinations
Which of the following is	s not chelating agent?	(1) I > II > III	Coordination Compounds 7.103 (2) III > II > I
Which of the Which	(2) Oxalato	(3) II > I > III	(4) II = I > III
(2) Glycmate	(4) Ethylene diamine	49. Increasing order EAN of	the metals in
The solution of AgBr in contains mainly the catio	presence of large excess of NH <sub>3</sub>	I. $[Ni(CN)_4]^{2-}$	II. $[Fe(CN)_6]^{3-}$
ontains manny the early	(2) A - (2)	III. $[Cu(CN)_4]^{3-}$ is	-10 [1 0(C14) <sub>6</sub> ]
$ \begin{array}{c} \text{conne} \\ \text{(1) NH}_{4}^{\oplus} \\ \text{(3) [Ag(NH_{3})]}^{\oplus} \end{array} $	$(2) Ag^{\oplus}$	(1) I < II < III	$(2) I \leq II = III$
(3) [Ag(1423)]	$(4) \left[ Ag(NH_3)_2 \right]^{\oplus}$	(3) I < III < II	(4)
Which of the following	species is not expected to be a	<b>50.</b> EAN of Na[PtCl <sub>3</sub> ( $\eta^2$ -C <sub>2</sub> H	$I_4$ )] is
112411		(1) 86	(2) 78
(1) NO	(2) NH <sub>4</sub> ⊕	(3) 84	(4) 34
$ (3) NH_2 - NH_3^{\oplus} $	(4) CO	<b>51.</b> EAN of [Fe( $\eta^2$ -C <sub>5</sub> H <sub>5</sub> ) (C	O) <sub>2</sub> CI]:
The number of donor site	es in dimethyl glyoxime, glycinato,	(1) 36	(2) 35
diethylene triamine and 1 (1) 2, 2, 3 and 4		(3) 37	(4) 34
(1) 2, 2, 3 and 4 (3) 2, 2, 2 and 6	(2) 2, 2, 3 and 6	52. Which has maximum EA	
(3) 2, 2, 2 and 6	(4) 2, 3, 3 and 6	(Cr = 24, Co = 27, Fe = 2)	6, Ni = 28)
Which of the following i		(1) $[\mathbf{Cr}(\mathbf{EDTA})]^{\Theta}$	$(2)[\mathbf{Co(en)}_{3}]^{3+}$
(1) Alum (3) Microcosmic salt	(2) Chrome alum	(3) $[Ni(CN)_4]^{2-}$	$(4)[\mathbf{Fe}(C_2O_4)_3]^{3-}$
(- /	(4) All of these	<b>53.</b> Give EAN value of Mg i	n [Mg(EDTA)] <sup>2–</sup> :
ions produced is	solved in water the total number of	(1) 16	(2)20
(1) Four	(2) E' 1.	(3) 22	(4) 18
(3) Ten	(2) Eight	<b>54.</b> EAN of cobalt is 36 in [O	$Co(NH_3)_2O_2(en)Br$ ]. Thus, $O_2$ is
	(4) Thirty-two	(1) dioxide	(2) superoxide ion
a complex ion?	statements is correct with regard to	(3) peroxide ion	(4) oxide
•	sts of a central ion bonded to two or	<b>55.</b> EAN of Fe in $[Fe(C_2O_4)]$	$_{3}$ ] <sup>3-</sup> is
more donor ions or m	olecules, usually does not dissociate	(1) 27	(2) 24
into simple ions or	molecules even in a solution, and	(3) 35	(4) 29
	ifferent from its constituent ions or	<b>56.</b> The EAN of Fe atom in	$(CO)_3$ Fe — Fe(CO); is
molecules.			\ /
	nolecules which coordinate with the		$(CO)_3$
	a complex are called ligands.	(1) 34	(2) 35
(3) The sum of the numb	er of electrons present in the central	(3) 36	(4) 37
metal ion or atom a	nd those donated by the ligands is atomic number of the central metal	Isomerism	
atom and this number	er is usually the same as the atomic	<b>57.</b> [Co(NH <sub>2</sub> ) <sub>6</sub> ] [Cr(CN) <sub>6</sub> ] a	nd $[Cr(NH_3)_6][Co(CN)_6]$ are
number of the next h	igher noble gas.	(1) Linkage isomers	(2) Ionisation isomers
(4) All of these		(3) Coordination isomers	(4) None of these
46. How many moles of Ag	Cl would be obtained, when 100 mL s treated with excess of AgNO <sub>3</sub> ?	58. The type of isomerisi chromium(III) perchlora	m present in pentaammine nitro
(1) 0.01	(2) 0.02	(1) Optical	(2) Linkage
(3) 0.03	(4) None of these	(3) Hydrate	(4) Polymerisation
$47. 0.001 \text{ mol of } Cr(NH_3)$	) <sub>5</sub> (NO <sub>3</sub> )(SO <sub>4</sub> ) was passed through the acid coming out of it required	isomers?	owing has the largest number of
a cation exchanger and	OH for neutralisation. Hence, the	(1) $[\operatorname{Cr(en)}_2\operatorname{Cl}_2]^{\oplus}$	(2) [Cr(NH <sub>3</sub> ) <sub>5</sub> Cl] <sup>2+</sup> (4) [lr(PR <sub>3</sub> ) <sub>2</sub> H(CO)] <sup>2+</sup>
001		$(3) \left[ \text{Ru}(\text{NH}_3)_4 \text{Cl}_2 \right]^{\oplus}$	(4) $[Ir(PR_3)_2H(CO)]^{2+}$
(1) [C-OIII ) SO 1NO	(2) $[Cr(NH_3)_5NO_3]SO_4$	<b>60.</b> [Cr(NH <sub>3</sub> ) <sub>5</sub> NO <sub>2</sub> ]SO <sub>4</sub> and	[Cr(NH <sub>3</sub> ) <sub>5</sub> ONO]SO <sub>4</sub> are related to
(3) $[Cr(NH_3)_5]$ (SO <sub>4</sub> ) (N	$IO_3$ ) (4) None of these	each other as:	(2)
(3) [CI(1113/5] (3 3 4)	٠٠	(1) Geometrical isomers	(2) Linkage isomers
Effective Atomic Number	(EAN)	(3) Coordination isomers	
48. Among the following,	select the order of decreasing EAN	isomerism if complexes	ing will be able to show geometrical are square planar?
values	II. $[Cr(CO)_6]^{\Theta}$	(1) Ma <sub>4</sub>	(2) Ma <sub>3</sub> b
I. $[Cr(CO)_6]$	II. [Cr(CO)6]	$\begin{array}{c} (1) \operatorname{Ma}_4 \\ (3) \operatorname{Mabcd} \end{array}$	(4) [M(AA)2]
III. $[Cr(CO)_6]^{\oplus}$		(5) 2	- 2-

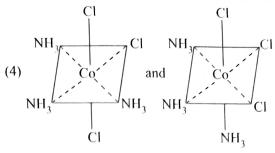
<ul><li>7.104 Inorganic Chemistry</li><li>62. The number of geometric</li></ul>	rical and ontical isomore of	72 Which of the following	will show a st
<b>62.</b> The number of geometrical and optical isomers of $[Cr(NH_3)_3(NO_3)_3]$ is		73. Which of the following will show optical isomerism?	
(1) 3	(2) 2	(1) $[ZnCl_4]^{2-}$ (3) $[Cr(C_2O_4)_3]^{3-}$	(2) [Cu(NH <sub>2</sub> ),] <sup>2+</sup>
(3) 0	(4) 4	(3) $[CI(C_2O_4)_3]$	(4) $[Co(CN)_{6}]^{3-}$
<b>63.</b> Both geometrical and optical isomerisms are shown by		74. In which of the following pairs both the complexes sh	
(1) $[Co(en)_2l_2]^{\oplus}$	(2) $[Co(NH_3)_2I]^{2+}$	(1) cis- $[Cr(C_2O_4)_2Cl_2]^{3-}$ ,	cis-[Co(NIII
(3) $[Cr(OX)_3]^{3-}$	(4) $[Co(NH_3)_4 l_3]^{\oplus}$	(2) $[Co(en)_3]Cl_3$ ,	cis- $[Co(NH_3)_4Cl_2]$ cis- $[Co(en)_2Cl_2]Cl_2$
	comprism shown is	(3) $[Co(NO_3)_3(NH_3)_3]$ ,	$\frac{\text{cis-[Pt(en)}_2\text{Cl}_2]\text{Cl}}{\text{cis-[Pt(en)}_2\text{Cl}_2]}$
<b>64.</b> In $[Co(C_2O_4)_3]^{3-}$ , the isomerism shown is (1) Ligand (2) Ontical		(4) [PtCl(en)Cl].	
(3) Geometrical	(2) Optical	75. Which of the following isomers?	g gives the maximum
	(4) Ionisation		
<b>65.</b> Which of the following octahedral complex does not show geometrical isomerism (A and B are monodentate ligands)?		(1) $[Co(NH_3)_4l_2]$ (3) $[Ni(C_2O_4)(en)_2]$	(2) [Ni(en)(NH <sub>3</sub> ) <sub>4</sub> ] <sup>2+</sup>
(1) [MA3B3]	$(2) [MA_4B_2]$	(3) $[Ni(C_2O_4)(en)_2]$	(4) $[Cr(SCN)_2(NH_3)_4]^{\oplus}$
(3) [MA <sub>5</sub> B]	$(4) \left[ MA_2B_4 \right]$	76. The possible number of (1) 6	optical isomers in [Cr(en), Cl 19
3 -	mers is associated with which one of	(1) 6 (3) 4	(2) 3
the following complex			(4) 2
(1) [M(AA)2]	$(2) [MA_3B_3]$	77. Which of the following (1) [Co(en) ] Pr	does not have optical isomers?
(3) [MABCD]	(4) [M(AA) <sub>3</sub> ]	$(1) [Co(en)_3] Di_3$	$(2)[Co(NH_2)_2Br_2]$
•	possible coordination isomer for the	(3) [Co(en) <sub>2</sub> Br <sub>2</sub> ]Br	(4) $[Co(en)(NH_3)_2Br_2]Br$
given compound [ $Pt(NH_3)_4Br_2$ ] [ $PtBr_4$ ] is		78. Which of the following will give a pair of enantiomorphs (1) $[Cr(NH_3)_6][Co(CN)_6]$ (2) $[Co(en)_6]$ Cl. [Cl.	
(1) 2	(2) 4	(3) $[Pt(NH_3)_4] [PtCl_6]$	$J = (2)[Co(en),Cl_{2}]Cl$
(3) 5	(4) 3	79 Roth $Cr^{3+}$ and $Pt^{4+}$ have	$(4) \left[ \text{Co(NH}_3)_4 \text{Cl}_2 \right] \text{NO}_2$
<b>68.</b> The following complexes are given		79. Both Cr <sup>3+</sup> and Pt <sup>4+</sup> have a coordination number of 6. Whi of the following pairs of complexes will show approximate	
1. $trans-[Co(NH_3)_4l_2]^{\oplus}$	2. $cis$ -[Co(NH <sub>3</sub> ) <sub>2</sub> (en) <sub>2</sub> ] <sup>3+</sup>	the same electrical conductance for their 0.1 M aqueo	
3. $trans-[Co(NH_3)_2(en)_2]^{3+}$		solutions:	
4. $[Nil_4]^{2-}$	2-	(1) CrCl <sub>3</sub> ·4NH <sub>3</sub> and PtCl <sub>3</sub>	₄·4NH₃
5. $[TiF_6]^{2-}$		(2) $CrCl_3 \cdot 3NH_3$ and $PtCl_4 \cdot 5NH_3$	
<b>6.</b> $[CoF_6]^{3-}$		(3) $CrCl_3 \cdot 6NH_3$ and $PtCl_4 \cdot 5NH_3$	
Choose the correct code.		(4) CrCl <sub>3</sub> ·5NH <sub>3</sub> and PtCl <sub>4</sub> ·6NH <sub>3</sub>	
(1) 4, 5 are coloured; 6 is colourless		<b>80.</b> Select the correct statement for [M(AB)b <sub>3</sub> cd]:	
(2) 2 is optically active; 1, 3 are optically inactive		(1) All geometrical isomers are optically active.	
(3) 1, 2 are optically active; 3 optically inactive		(2) It has four trans isomer with respect to b.	
(4) 4 is coloured; 5, 6 are colourless		(3) It has seven geometrical isomers.	
69. The following represents a pair of enantiomers:		(4) It has three cis and two trans isomers with respect to b.	
(1) trans- $[\operatorname{Crl}_2 \operatorname{en}_2]^{\oplus}$ (2) cis- $[\operatorname{Crl}_2 \operatorname{en}_2]^{\oplus}$		81. Which one of the following coordination compound	
(3) trans- $[\operatorname{Crl}_2(\operatorname{NH}_3)_4]^{\oplus}$	$(2) \operatorname{cis}_{2} \operatorname{en}_{2} \operatorname{en}_{2}$	exhibits ionisation isome	
The compound [Dep., Ar	(4) cis-[Crl <sub>2</sub> (NH <sub>3</sub> ) <sub>4</sub> ] <sup>©</sup>	(1) $[Cr(NH_3)_6]Cl_3$	$(2) \left[ Cr(en)_3 Cl_3 \right]$
The compound [PtBr <sub>2</sub> (N]		$(3) \left[ Cr(en)_3 \right] Cl_3$	(4) $[Co(NH_3)_5Br]SO_4$
(1) Geometrical isomers	(2) Coordination isomers	82. Which of the following	g complex compounds exhibit
(3) Optical isomers	(4) Linkage isomers	cis-trans isomerism?	(a) In ICI D.II
The compound [CrCl <sub>2</sub> (N)	$H_3$ <sub>2</sub> (en)] can form	(1) $[PtCl_2(NH_3)_2]$	(2) [PdCl <sub>2</sub> Brl]
(1) Geometrical isomers	(2) Coordination isomers	(3) [Pt(NH <sub>3</sub> ) (py) (Cl) (Bi	(4) All of these
(3) Optical isomers	(4) Linkage isomers	83. How many geometrical i	somers are possible for the square
One mole of complex compound Garage		planar complex [Pt(NO <sub>2</sub> ) (1) Four	$(py)(NH_3)(NH_2OH)JHO_2$ (2) Five
		(3) Fight	(4) Three
complex reacts with two moles of AgNO <sub>2</sub> to yield two moles		84. Consider the following	anatial arrangements of the
of rigor <sub>(s)</sub> . The complex is		octahedral complex ion [6]	So(NH <sub>2</sub> ).Cl <sub>2</sub> 1 <sup>\theta</sup> .
1) $[Cr(NH_3)_4Cl]Cl_2\cdot NH_3$	(2) $[Cr(NH_3)_4Cl_2]Cl\cdot NH_3$	octanicara complex fon [C	20(14113/4212)
3) [Cr(NH <sub>3</sub> ) <sub>5</sub> Cl]Cl <sub>2</sub>	(4) $[Cr(NH_3)_3Cl_3] \cdot 2NH_3$		
3 3 2	3/331 21113		



Which of the following statements is incorrect regarding these structures?

- (1) I and II are enantiomers
- [2] II and III are cis and trans isomers respectively
- 3) III and IV are trans and cis isomers respectively
- (4) II and IV have identical structures.
- & Which of the following pairs of structures represent facial and meridional isomers (geometrical isomers) respectively?





- **86.** Which would exhibit coordination isomerism?
  - (1)  $[Cr(NH_3)_6][Co(CN)_6]$
- (2)  $[Cr(en)_2Cl_2]^{\oplus}$
- $(3) [Cr(NH_3)_6]Cl_3$
- (4) [Cr(edta)]
- **87.** Which would exhibit ionisation isomerism?
  - (1)  $[Co(NH_3)_6][(C_2O_4)_3]$
- (2)  $[Co(NH_3)_5Br]^{2+}SO_4^{2-}$
- (3)  $K_3[Fe(CN)_6]$
- (4)  $K_3[Fe(C_2O_4)_3]$
- 88. The water-soluble complex among the following is
  - (1)  $[Ni(HDMG)_2]$
- (2)  $[Co(NH_3)_3Cl_3]$
- $(3) Ni(CO)_4$
- (4) [Ni(HDMG)<sub>2</sub>]Cl<sub>2</sub>
- 89. Arrange the following optical activity possible in
  - (1)  $[Co(H_2O)_2(NH_3)_3Cl]^{\oplus}$
- (2)  $[Co(H_2O)_4Cl_2]^{\oplus}$
- (3)  $[Co(NH_3)_4(NO_2)Cl]^{\oplus}$
- (4)  $[Co(CN)_5NC]^{\Theta}$
- 90. When an excess of ammonia solution is added to CuSO<sub>1</sub> which solution is formed?
  - (1)  $\left[ \text{Cu(NH}_3)_7 \right]^{2+}$
- (2)  $\left[\operatorname{Cu}(\operatorname{NH}_3)_4\right]^{\oplus}$
- (3)  $\left[\operatorname{Cu}(\operatorname{NH}_3)_2\right]^{\oplus}$
- (4)  $[Cu(NH_3)_4]^{2}$
- 91. Copper sulphate solution reacts with KCN to give
  - $(1) Cu(CN)_2$
- (2) CuCN
- (3)  $K_2[Cu(CN)_4]$
- (4)  $K_3[Cu(CN)_4]$
- **92.** The ionisation isomer of [Co(H,O)<sub>4</sub>Cl(NO<sub>2</sub>)]Cl is
  - (1)  $[Co(H_2O)_4(NO_2)]Cl_2$
- (2)  $[Co(H_2O)_4Cl_2]NO_2$

- (3)  $[Co(H_2O)_4Cl(ONO)]Cl$  (4)  $[Co(H_2O)_4Cl_2(NO_2)]\cdot H_2O$
- 93. The 0.0001 molal solution of a complex  $AB_{10}$  has the freezing point of -0.0015°C in water. Assuming 100% dissociation of the complex, find the proper representation of the complex.  $[K_1(H_2O = 1.86 \text{ Km}^{-1})]$ 
  - $(1)[AB_8]$
- $(2) [AB_3]B_7$
- $(3) [AB_7] B_3$
- $(4) [AB_5] B_5$
- 94. From the information given in the passage, what is the most likely configuration of the cobalt d-electrons for the species (A)  $CoCl_6^{3-}$  and (B)  $Co(NO_2)_6^{3-}$ ?
  - (1) both (A) and (B) have low spin
  - (2) (A) has high spin; (B) has low spin
  - (3) (A) has low spin; (B) has high spin
  - (4) Both (A) and (B) have high spin
  - 95. The hybridisation states of the central atom ion in the complex ions  $[FeF_6]^{3c}$ ,  $[Fe(H_2O)_6]^{3+}$  and  $[Ni(NH_3)_6]^{2+}$  are:
    - (1)  $sp^3d^2$ ,  $dsp^2$  and  $d^4s^2$  respectively
    - (2) all  $3d^2 4s 4p^3$
    - (3) all  $4s 4p^3 4d^2$
    - (4)  $sp^3d^2$ ,  $dsp^3$  and  $p^4d^2$  respectively

- **96.** Among (A)  $TiF_6^{2-}$ , (B)  $CoF_6^{3-}$ , (C)  $Cu_2Cl_2$  and (D)  $NiCl_4^{2-}$  (atomic number of Ti = 22, Co = 27, Cu = 29, Ni = 28), the colourless species are:
  - (1) (B) and (D)
- (2) (A) and (B)
- (3) (C) and (D)
- (4) (A) and (C)
- 97. The magnetic moment of a complex ion is 2.83 BM The complex ion is:
  - (1)  $[Cr(H_2O)_c]^{3+}$
- (2)  $[Cu(CN)_6]^2$
- $(3) [V(H_2O)_6]^{3+}$
- (4)  $[MnCl_4]^{2-}$
- 98. Which of the following statements is not true for the reaction given below?

$$[Cu(H_2O)_6]^{2+} + 4NH_3 \Longrightarrow [Cu(NH_3)_4]^{2+} + 4H_2O$$

- (1) It is a ligand-substitution reaction
- (2) NH, is a relatively strong-field ligand while H<sub>2</sub>O is a weak field ligand.
- (3) During the reaction, there is a change in colour from light blue to dark blue.
- (4) [Cu(NH<sub>3</sub>)<sub>4</sub>]<sup>2+</sup> has a tetrahedral structure, and is paramagnetic.

# Hybridisation, Magnetic and Optical Properties

- **99.** The *d*-electron configurations of  $Mn^{2+}$ ,  $Fe^{2+}$ ,  $Co^{3+}$  and  $Ni^{2+}$ are  $3d^5$ ,  $3d^6$ ,  $3d^6$ ,  $3d^8$ , respectively. Which of the following aqua complexes will exhibit the minimum paramagnetic behaviour?
  - (1)  $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$
- (2)  $[Co(H_2O)_6]^{3+}$
- $(3) [Mn(H_2O)_6]^{2+}$
- (4)  $[Ni(H_2O)_6]^{2+}$
- 100. Which of the following is paramagnetic?
  - (1) [Fe(CO)<sub>5</sub>]
- (2) [Cr(CO)<sub> $\epsilon$ </sub>]
- $(3) [Fe(CN)_6]^4$
- (4)  $[Cr(NH_2)_c]^{3+}$
- 101. The pair in which both species have same magnetic moment (spin only value) is
  - (1)  $I[Cr(H_2O)_6]^{2+}$ ,  $[CoCl_4]^{2-}$
  - (2)  $[Cr(H_2O)_6]^{2+}$ ,  $[Fe(H_2O)_6]^{2+}$
  - (3)  $[Mn(H_2O)_6]^{2+}$ ,  $[Cr(H_2O)_6]^{2+}$
  - (4)  $[CoCl_4]^{2-}$ ,  $[Fe(H_2O)_6]^{2+}$
- 102. Select the correct order of magnetic moment (in BM) from the following options:
  - I.  $[MnCl_4]^{2-}$
- II.  $[CoCl_4]^{2-}$  III.  $[Fe(CN)_6]^{4-}$
- (1) 1 > 11 > 111
- (2) III > II > I
- (3) III > I > II
- $(4) I > \coprod > \coprod$
- 103. Which of the pair of complex compounds are tetrahedral as well as diamagnetic?
  - (1)  $[CoCl_4]^{\odot}$  and  $[Co(CO)_4]^{\odot}$
  - (2)  $[Ag(SCN)_4]^2$  and  $[NiCl_4]^2$
  - (3)  $[Co(CO)_4]^{\odot}$  and  $[Ni(CN)_4]^4$
  - (4)  $[PdCl_4]^{2-}$  and  $[Ni(CN)_4]^2$
- 104. Which of the following has a square planar geometry?
  - $(1) [Ptl_{4}]^{2-}$
- (2)  $[Col_4]^{2}$
- (3)  $[Fel_{4}]^{2-}$
- (4)  $[Nil_4]^2$
- **105.** Among  $[Ni(CO)_4]$ ,  $[Ni(CN)_4]^{2-}$  and  $[NiBr_4]^{2-}$  species, the hybridisation state of Ni atoms are respectively:

- (1)  $sp^3$ ,  $ds^2p$ ,  $dsp^2$
- (2)  $sp^3$ ,  $dsp^2$ ,  $sp^3$
- (3)  $dsp^2$ ,  $sp^3$ ,  $sp^3$
- $(4) sp^3, sp^3, dsp^2$
- 106. Arrange the following in order of decreasing number of
  - I.  $[Fe(H_2O)_6]^{2+}$
- II. [Fe(CN)<sub>6</sub>]<sup>3</sup>-
- III. [Fe(CN)<sub>6</sub>]<sup>4</sup> (1) IV, I, II, III
- II.  $[Fe(H_2O)_6]^{3+}$ (2) J, II, III, IV
- (3) III, II, I, IV
- (4) II, III, I, IV
- 107. A substance which is not paramagnetic is
  - (1)  $Cr(ClO_4)_3$
- (2) KMnO<sub>4</sub>
- (3) TiCl<sub>2</sub>
- (4) VOB $r_2$
- 108. Which of the following statements is correct?
  - (1)  $[NiCl_4]^{2-}$  complex is more stable than  $[Ni(dmg)_2]$  due to higher CFSE value.
  - (2) With  $d^2sp^3$  hybridisation  $[FeCl(CN)_4(O_2)]^4$  complex is diamagnetic.
  - (3)  $[V(CO)_6]$  is not very stable and easily reduces to  $[V(CO)_6]^{\Theta}$ .
  - (4) Ligands such as CO,  $CN^{\Theta}$ ,  $NO^{\oplus}$  are  $\pi$  electron donor due to the presence of filled  $\pi$ -molecular orbital.
- 109. An aqueous solution of titanium bromide shows zero magnetic moment. Assuming the complex as octahedral in aqueous solution, the formula of the complex is
  - (1)  $[TiBr_6]^{3-}$
- (2)  $[Ti(H_2O)_6]Br_4$
- (3)  $[TiBr_{\epsilon}]^{2-}$
- (4)  $[Ti(H_2O)_4 Br_2]$
- 110. Geometry, hybridisation and magnetic moment of the ions  $[Ni(CN)_4]^{2-}$ ,  $[MnBr_4]^{2-}$ , and  $[FeF_6]^{3-}$ , respectively are
  - (1) Tetrahedral, square planar, octahedral:  $dsp^2$ ,  $sp^3$ ,  $sp^3d^2$ : 0, 5.9, 4.9.
  - (2) Tetrahedral, square planar, octahedral:  $sp^3$ ,  $dsp^2$ ,  $sp^3d^2$ : 5.9, 0, 4.9.
  - (3) Square planar, tetrahedral, octahedral:  $dsp^2$ ,  $sp^3$ ,  $d^2sp^3$ : 5.9, 4.9, 0
  - (4) Square planar, tetrahedral, octahedral:  $dsp^2$ ,  $sp^3$ ,  $sp^3d^2$ : 0, 5.9, 4.9
- 111. The correct order of magnetic moment (spin values in BM) is (Atomic number Mn = 25, Fe = 26, Co = 27)
  - I.  $[MnBr_4]^{2-}$  II.  $[Fe(CN)_6]^{4-}$  III.  $[CoBr_4]^{2-}$ 
    - (1) || > || > 1
- (2) I > II > III
- (3) II > I > III
- (4) I > III > II
- 112. A square planar complex is formed by hybridisation of which atomic orbitals?
  - (1)  $s, p_x, p_y, d_{yz}$
- $(2) s, p_y, p_y, d_{y^2-y^2}$
- (3)  $s, p_y, p_z, d_{xy}$
- $(4) s, p_{y}, p_{y}, d_{z2}$
- 113. The colour of a complex compound is due to:
  - (1) Promotion of 3*d*-electrons of the central atom/ion to 4*p*-orbitals
  - (2) Promotion of 3*d*-electrons of the central atom/ion to 4s-orbitals
  - (3) Promotion of 3*d*-electrons of the central atom/ion within *d*-orbitals
  - (4) Promotion of 4s-electrons of the central atom/ion to 4p-orbitals

transition-metal compound absorbs violet-indigo if a absorbs viol

(1) Green

(2) Yellow

(3) Orange

(4) Blue

(3) on metal compounds are usually coloured. This is the tothe electronic transition: to the electronic transition:

(1) From d-orbital to s-orbital

(1) From p-orbital to s-orbital

 $^{(r)}_{(3)}$  From d-orbital to p-orbital

 $\frac{(3)}{(4)}$  Within the *d*-orbitals

Which of the following compound is not coloured?

"(1) Na<sub>2</sub>[CuCl<sub>4</sub>]

(2)  $Na_{5}[CdCl_{4}]$ 

 $_{(3)}K_4[Fe(CN)_6]$ 

(4) K<sub>3</sub>[Fe(CN)<sub>6</sub>]

The colour of Cu<sup>®</sup> compound is

(1) White

(2) Blue

(3) Orange

(4) Yellow

# (CFT)

Which of the following complex has higher  $\Delta_0$  value?

 $(1) [Fe(H_2O)_6]^{2+}$ 

(2)  $[Fe(H_2O)_6]^3$ 

(3)  $[Fe(CN)_6]^{3-}$ 

(4) All have equal

19. Relative to the average energy in the spherical crystal field, the  $t_{2\sigma}$  orbitals in tetrahedral field is

(1) Raised by  $(2/5) \Delta_t$ 

(2) Lowered by  $(2/5) \Delta_t$ 

(3) Raised by  $(3/5) \Delta_t$ 

(4) Lowered by  $(1/5) \Delta_t$ 

120. The crystal field splitting energy for octahedral  $(\Delta_0)$  and tetrahedral ( $\Delta_t$ ) complexes is related as:

 $(1) \Delta_t = \frac{4}{9} \Delta_0$ 

 $(2)\,\Delta_{\rm t} = \frac{1}{2}\,\Delta_{\rm o}$ 

 $(3) \Delta_0 = -2\Delta_t$ 

$$(4)\,\Delta_0 = -\frac{4}{9}\,\Delta_t$$

12L[Cr(H<sub>2</sub>O)<sub>6</sub>]Cl<sub>3</sub> (atomic number of Cr = 24) has a magnetic moment of 3.83 BM. The correct distribution of 3d-elections in the chromium present in the complex is

(1)  $3d^{1}_{xy}$ ,  $3d^{1}_{yz}$ ,  $3d^{1}_{zx}$  (2)  $3d^{1}_{xy}$ ,  $3d^{1}_{yz}$ ,  $3d^{1}_{z^{2}}$ 

 $(3) 3d^{1}_{(x^{2}-y^{2})}, 3d^{1}_{z^{2}}, 3d^{1}_{z^{2}}$ 

(4) 
$$3d^{1}_{xy}$$
,  $3d^{1}_{(x^{2}-y^{2})}$ ,  $3d^{1}_{xz}$ 

122. In which of the following coordination entities, the magnitude of  $\Delta_0$  [CFSE in octahedral field] will be maximum?

(1)  $[Co(CN)_6]^{3-}$ 

(2)  $[CoF_6]^{3-}$ 

(3)  $[Co(NO_2)_6]^{3-}$ 

(4)  $\left[\text{Co(NH}_3)_6\right]^{3+}$ 

123. In which of the following configurations will there be the possibility of both para and diamagnetism, depending on the nature of the ligands?

 $(1) d^3$ 

(2)  $d^7$ 

 $(3) d^6$ 

124. For Mn<sup>3+</sup> ion, the electron pairing energy P is about  $28,000 \text{ cm}^{-1}, \Delta_0 \text{ values for the complexes } [\text{Mn}(\text{H}_2\text{O})_6]^{3+}$  and  $[Mn(CN)_6]^{3-}$  are 15,800 cm<sup>-1</sup> and 38,500 cm<sup>-1</sup> respectively, which of the following complex is high spin:

(1) Both are high spin

(2)  $[Mn(H_2O)_6]^{3+}$ 

(3)  $[Mn(CN)_6]^{3-}$ 

(4) None of these

125. Which of the following ligands are correctly represented in an spectrochemical series?

 $(1) SCN^{\Theta} < F^{\Theta} < CN^{\Theta}$ 

(2)  $SCN^{\Theta} < CN^{\Theta} < F^{\Theta}$ 

(3)  $F^{\Theta} < SCN^{\Theta} < CN^{\Theta}$ 

(4)  $F^{\Theta} < CN^{\Theta} < SCN^{\Theta}$ 

126. The increasing order of the crystal field splitting power of some common ligands is

(1)  $NH_3 \le NO_2^{\Theta} \le CN^{\Theta} \le H_2O$ 

(2)  $H_2O < NO_2^{\Theta} < CN^{\Theta} < NH_2$ 

(3)  $H_2O < NH_2 < NO_2^{\Theta} < CN^{\Theta}$ 

(4)  $H_2O \le NH_3 \le CN^{\Theta} \le NO_2^{\Theta}$ 

127. The value of "spin only" magnetic moment for one of the following configuration is 2.84 BM. The correct one is

(1)  $d^4$  (in strong field ligand)

(2)  $d^2$  (in weak field ligand)

(3)  $d^3$  (in weak as well as in strong field ligand)

(4)  $d^5$  (in strong field ligand)

128. The complexion which has no d-electron in the central metal atom is

 $(1) [MnO_{4}]^{\Theta}$ 

(2)  $[Co(NH_3)_6]^{3+}$ (4)  $[Cr(H_2O)_6]^{3+}$ 

(3)  $[Fe(CN)_2]^{3-}$ 

129. Which of the following statements is correct for the complex  $Ca_2[Fe(CN)_5O_2]$  having  $t_{2g}^6$ ,  $e_g^0$  electronic configuration?

(1)  $d^2sp^3$  hybridised and diamagnetic

(2)  $sp^3d^2$  hybridised and paramagnetic

(3)  $sp^3d^2$  hybridised and diamagnetic

(4)  $d^2sp^3$  hybridised and paramagnetic

130. Which of the following complex is inner orbital as well as low spin complex?

(1)  $\left[ \text{Cr}(\text{H}_2\text{O})_6 \right]^{3+}$ 

(2)  $[Fe(CN)_6]^{3-}$ 

(3)  $[Cu(CN)_4]^{3-}$ 

(4)  $[Mn(NH_2)_c]^{2+}$ 

131. The magnetic moment of a certain complex (A) of Co was found to be 4.89 BM and the EAN as 36. Co also forms complex (B) with magnetic moment 3.87 BM and EAN as 37, and complex (C) with EAN as 36 but diamagnetic. Which of the following statements is true regarding the above observation?

(1) The oxidation states of Co in (A), (B) and (C) are +3, +2 and +3, respectively.

(2) Complexes (A) and (B) have  $sp^3d^2$  hybridisation state while (C) has  $dsp^3$  hybridisation state.

(3) The spin multiplicities of Co in (A), (B) and (C) are 3, 2 and 1, respectively.

(4) The oxidation states of Co in (A), (B) and (C) are +6, +8 and +1, respectively.

132. Spin only magnetic moments of a  $d^8$  ion in octahedral, square planar, and tetrahedral complexes, respectively, are

(1) 2.8 BM, 0 and 2.8 BM

(2)0, 0 and 0 BM

(3) 2.8, 2.8 and 2.8 BM

(4) None of these

133. Given the following data about the absorption maxima of several complex ions, what is the order of  $\Delta_0$  for these ions?

Compound	1
I. $\left[\text{CrCl}_{6}\right]^{3-}$	λ <sub>max</sub> 758
II. $[Cr(NH_3)_6]^{3+}$	465
III. $[Cr(H_2O)_6]^{3+}$	694

### 7.108 Inorganic Chemistry $(1) \Delta_0(I) < \Delta_0(II) < \Delta_0(III)$ $(2) \Delta_0(II) \le \Delta_0(III) \le \Delta_0(I)$ $(3) \Delta_0(I) \le \Delta_0(III) \le \Delta_0(II)$ 144. Which bond properties are consistent with one another? $(4) \Delta_0(III) \le \Delta_0(II) \le \Delta_0(I)$ **134.** Predict the order of $\Delta_0$ for the following compounds: II. $[Fe(CN),(H,O)_4]$ I. $[Fe(H_2O)_6]^{2+}$ III. $[Fe(CN)_4(H_2O)_5]^2$ $(1) \Delta_0(I) \le \Delta_0(II) \le \Delta_0(III) \quad (2) \Delta_0(II) \le \Delta_0(I) \le \Delta_0(III)$ $(3) \Delta_0(III) \le \Delta_0(II) \le \Delta_0(I) \quad (4) \Delta_0(II) \le \Delta_0(III) \le \Delta_0(I)$ 145. Select the correct order of C-O bond order in mixed 135. Among the following pairs of complexes, in which case the $\Delta_0$ value is higher for the second compound. (1) $[Co(H,O)_6]^{3+}$ , $[Rh(H,O)_6]^{3+}$ (2) $[Co(NH_3)_6]^{3+}$ , $[CoCl_6]^{3-}$ (3) $[Co(H_2O)_6]^{3+}$ , $[Co(H_2O)_6]^{2+}$ (4) $[Co(CN)_6]^{3-}$ , $[Co(NH_3)_6]^{3+}$ 146. Compare C-C bond length (x) of C<sub>2</sub>H<sub>4</sub> in Zeise's salt and 136. Which of the following complexes have high stability constant $(k_s)$ value. (1) $[Pt Br_{4}]^{3}$ (2) $[Pt(NH_2)Br_2]^{\Theta}$ (4) $[Pt (NH_2)_4]^{2+}$ (3) $[Pt (NH_3)_3Br]^{\oplus}$ 137. The complex ion having minimum wavelength of absorption in the visible region is: (2) Trans-[Cr Br<sub>2</sub> (NH<sub>3</sub>)<sub>4</sub>] $^{\oplus}$ (1) Cis-[Cr Br, $(NH_3)_A$ ] $^{\oplus}$ (3) $[Cr(NH_3)_6]^{3+}$ (4) $[\text{Cr Br (NH}_3)_5]^{2+}$ 138. Select the pairs having green and violet colour respectively. (1) (I) $[Cr(H_2O)_6]Br_3$ ; (II) $[Cr(H_2O)_4Br_2]Br. 2H_2O$ (2) (I) $[Cr(H_2O)_6]Br_2$ ; (II) [Cr(H<sub>2</sub>O)<sub>6</sub>]Br<sub>3</sub>(3) (I) $[Cr(ONO)(H_2O)_5]Br_2$ (II) $[Cr(NO_2)(H_2O)]Cl_2$ (4) (I) [Pr Cl (NH<sub>3</sub>)<sub>3</sub>]NO<sub>2</sub>; (II) [Pt $(NO_2)(NH_3)_3$ ]Cl 139. Select incorrect match between compound and reason for its observed colour. (1) HgI<sub>2</sub>: Polarization (2) Ag<sub>2</sub>PO<sub>4</sub>: Polarization (3) [Fe(H<sub>2</sub>O)<sub>5</sub>NO]SO<sub>4</sub>: d-d transition (4) MnO<sub>4</sub> : charge transfer spectrum. **140.** If the colour of $[Ni(H_2O)_2(en)_2]^{2+}$ (I) is blue-purple then what would be the colour $g[Ni(en)_3]^{2+}(II)$ ? (1) Violet (2) Deep blue (3) Pale blue (4) Green 141. Which is the following compounds absorbs at shorter wavelength in visible spectrum? (1) [Cr Br<sub>3</sub> ( $H_2O$ )<sub>3</sub>].3 $H_2O$ (2) $[Cr Br_2(H_2O)_4]Br.2H_2O$ (3) [Cr Br $(H_2O)_5$ ]Br<sub>2</sub>. $H_2O$ (4) [Cr $(H_2O)_6$ ]Br<sub>3</sub>. 142. CFSE value for brown ring complex for test of NO<sub>3</sub> ion is $(1) -2.4 \Delta_0$ (2) $-1.8 \Delta_0$ $(3) -0.8 \Delta_0$ $(4) -0.4 \Delta_0$ Application of Coordination Compounds and Miscellaneous 143. Which of the following is incorrect about Wilkinson's

catalyst?

(1) It is a diamagnetic complex.

(3) x = y(4) None of these 147. Which of the following organometallic compound is a  $\sigma$  and  $\pi$ -bonded? (1)  $[Fe(\eta^5 - C_5H_5)_2]$ (2)  $K[PtCl_3(\eta^2-C_2H_4)]$ (3)  $[Co(CO)_5 NH_3]^{2+}$  $(4) [Fe(CH_2)_2]$ 148. Which of the following statement(s) is/are true or false?  $S_1$ : Complexes having  $d^0$  or  $d^{10}$  configuration of metal ions are always diamagnetic. S2: In organometallic compounds, carbon is bonded to metals directly. S<sub>3</sub>: In Fe(CO)<sub>5</sub>, the Fe—C bond possesses both  $\sigma$  and  $\pi$ characteristics. S<sub>4</sub>: Extra stability of metal carbonyls is explained by synergic bonding. (1) TTTT (2) FTFT (3) TTFF (4) FTTT 149. Which of the following complex can act as an oxidising agent as well as reducing agent?  $(1) \operatorname{Mn}(CO)_5$  $(2) Ti(CO)_6$  $(3) \text{ Mn(CO)}_{6}$ (4) None of these 150. Which of the following statements is correct for the [Fe(H<sub>2</sub>O)<sub>5</sub>NO]SO<sub>4</sub> complex? (1) The EAN value of Fe in this complex depends on the charge of NO ligand. (2) The EAN value of Fe in this complex does not depend on the charge of NO ligand. (3) The hybridisation of the central atom is  $d^2sp^3$ . (4) It is paramagnetic with  $\mu = 1.73$  BM 151. Which of the following is not considered as an organometallic compound? (1) Ferrocene (2) Cis-platin (4) Grignard reagent (3) Zeise's salt 152. Among the following, which is not the  $\pi$ -bonded órganometallic compound?

(2) It is a non-ionic complex.

(3) It is a tetrahedral complex.

phosphine carbonyl complex:

III.  $[Mo(PhCl_2)_3 (CO)_3]$ 

Bond order

(1) higher

(2) lower

(3) higher

(4) lower

(1) I > II > III

(3) I = II > III

(1) x > y

(4) It is very effective for selective hydrogenation of organic

Vibrational frequency

higher

lower

lower

higher

(2) I < II < III

(4) I < II > III

(2) v > x

molecule at room temperature and pressure.

Bond length

shorter

shorter

longer

longer

I.  $[Mo(Ph_3P)_3(CO)_3]$  II.  $[Mo(Ph_2PCI)_3(CO)_3]$ 

C-C bond length (y) of  $C_2(CN)_4$  in  $\overline{K}$  [PtCl<sub>3</sub>C<sub>2</sub>(CN)<sub>4</sub>]:

(2)  $[Cr(\eta^6 - C_6H_6)_2]$ 

(3) [Fe( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>]

(4) K[PtCl<sub>3</sub>( $\eta^2$ -C<sub>2</sub>H<sub>4</sub>)]

Mg is an important component of which biomolecule occurring extensively in living world?

(1) Haemoglobin

(2) Chlorophyll

(3) Florigen

(4) ATP

154. What is the shape of Fe(CO)<sub>5</sub> molecule and which of the following d-orbitals involved in hybridization?

(1) Tetrahedral  $d_{x^2-x^2}$ 

(2) Trigonal bipyramidal,  $d_{12,12}$ 

(3) Trigonal bipyramidal,  $d_{-2}$ 

(4) Square pyramidal

15 Among the properties (A) reducing, (B) oxidising, (C) complexing, the set of properties shown by CN ion towards metal species is

(1) B. C

(2) A, B, C

(3) C, A

(4) A, B

156. Ferrocene is

(1)  $[Fe(\eta^2 - C_6H_5),]$ 

(2)  $[Fe(\eta^5 - C_5H_5)_2]$ 

(3) [Fe( $\eta^6$ -C<sub>6</sub>H<sub>6</sub>)<sub>2</sub>]

(4)  $[Fe(\eta^3 - C_3H_3)_2]$ 

157. Dimethylglyoxime is coordinated to Ni<sup>2+</sup> through:

(1) Two oxygen atoms

(2) Two nitrogen atoms

(3) Two oxygen and one nitrogen atoms

(4) Two oxygen and two nitrogen atoms

158. In isolated condition C–C bond length of  $C_2H_4$  is x, than the bond length ofn C-C bond of C2H4 in Zeise's salt is

(1) Greater than x

(2) Less than x

(3) Equal to x

(4) None of these

159. When  $K_4[Fe(CN)_6]$  is treated with  $FeCl_3$ , a blue colour is obtained. It is due to the formation of

(1)  $\operatorname{Fe}^{\operatorname{II}}\left[\operatorname{Fe}^{\operatorname{III}}(\operatorname{CN})_{6}\right]^{\Theta}$ 

(2)  $\operatorname{Fe}^{\operatorname{III}} \left[ \operatorname{Fe}^{\operatorname{II}} (\operatorname{CN})_6 \right]^{\Theta}$ (4) None of these

(3) Both (a) and (b)

160. The common features among the species  $CN^{\Theta}$ , CO and NO<sup>⊕</sup> are

(1) bond order three and isoelectronic

(2) bond order three and weak field ligands

(3) isoelectronic and weak field ligands

(4) bond order two and  $\pi$ -acceptors

[6]. Consider the following complex:

[Co(NH<sub>3</sub>)<sub>5</sub>CO<sub>3</sub>]BrO

the coordination number, oxidation number, number of d-electrons and number of unpaired d-electrons of the metal are respectively:

(1) 6, 3, 6, 0

(2) 7, 1, 6, 4

(3) 7, 2, 7, 1

(4) 6, 2, 7, 3

The bond length of C-O bond in carbon monoxide is 1.128Å. The C–O bond in [Fe(CO)<sub>5</sub>] is

(l) 1.115 Å

(2) 1.128 Å

(3) 1.178 Å

(4) 1.150 Å

163. The most stable ion is

(1)  $[Fe(C_2O_4)_3]^3$ 

(2)  $[Fe(CI)_6]^3$ 

(3)  $[Fe(H_2O)_6]^{3+}$ 

(4)  $[Fe(SCN)_6]^3$ 

**164.** The number of  $\sigma$  and  $\pi$ -bonds in Fe<sub>2</sub>(CO)<sub>9</sub>, respectively, are

(1)  $22\sigma$  and  $15\pi$ 

(2)  $22\sigma$  and  $16\pi$ 

(3)  $23\sigma$  and  $15\pi$ 

(4)  $15\sigma$  and  $8\pi$ 

**165.** Ag<sup> $\oplus$ </sup> forms many complexes, some of these are  $[Ag(NH_3)_2]^{\oplus}$ ,  $2[Ag(CN)_2]^{\Theta}$ ,  $[Ag(S_2O_3)_2]^{3-}$ 

Which of the following statements is true?

(1) In these complexes, Ag<sup>⊕</sup> is a Lewis base

(2) The hybridisation of  $Ag^{\oplus}$  is  $sp^2$ .

(3) The Ag<sup>⊕</sup> complexes are good reducing agents

(4) These complexes are all linear

166. Hardness of water is estimated by simple complex formation titration. Complex formed by cation in hard water during estimation of hardness is

(2)  $Na_{2}[Mg(EDTA)]$ 

(1)  $Na_2[Ca(PO_3)_6]$ (3)  $[Ca(SO_4)_2]^{2-}$ 

(4) Na<sub>2</sub>[Pb(EDTA)]

**167.** The ligand called  $\pi$ -acid is

(1) CO

(2) C<sub>2</sub>O<sub>4</sub><sup>2-</sup> (4) ethylene

(3) NH<sub>2</sub>

168. The complex used as an anticancer agent is

(1) mer- $[co(NH_3)_3Cl_3]$  $(3) \text{Na}_{2}[\text{CoCl}_{4}]$ 

(2) cis-[PtCl<sub>2</sub>(NH<sub>2</sub>)<sub>2</sub>]

(4) cis- $K_2[Pt(Cl_2Br_2)]$ 169. Which is uses in cancer chemotherapy?

(1) cis-platin

(2) Zeisse's salt (4) None of these

(3) Both (a) and (b)

170. Zeise's salt is (1)  $Cr(\eta^6 - C_6H_6)_2$ 

(2)  $Fe(\eta^5 - C_5H_5)_2$ 

(3)  $K[Pt(\eta^2-C_2H_4)Cl_3]$ 

(4)  $K[Pt(\eta^2-C_2H_4)_2Cl_2]$ 

171. cis-diamminedichloridoplatinum(II),  $[Pt(NH_3)_2Cl_2]$ , is

$$\begin{bmatrix} H_3N \\ H_3N \end{bmatrix} Pt \begin{bmatrix} CI \\ CI \end{bmatrix}$$

One of the number of platinum coordination compound is used in the treatment of cancer. Commonly known as cis-platin, this compound has the ability to block the uncontrolled division of cancerous cells that results in the growth of tumours. Recent studies show that cisplatin can cause serious side effects, including severe kidney damage. cis-platin is replaced by which of the following compounds:

(1) 
$$\begin{bmatrix} \text{CI} \\ \text{H}_{3}\text{N} \end{bmatrix} \text{Pt} \underbrace{\begin{pmatrix} \text{NH}_{3} & \text{H}_{3}\text{N} \\ \text{NH}_{2}(\text{CH}_{2})_{n} - \text{H}_{2}\text{N} \\ \text{trans-isomer}(n-2 \text{ to 6}) \end{pmatrix}}_{\text{trans-isomer}(n-2 \text{ to 6})} \text{Pt} \underbrace{\begin{pmatrix} \text{CI} \\ \text{NH}_{3} \end{pmatrix}}_{\text{NH}_{3}}^{2}$$

(2) 
$$\begin{bmatrix} H_3N > Pt < Cl & Cl \\ H_3N > Pt < NH_2(CH_2)_n - H_2N > Pt < NH_3 \\ (n = 2 \text{ to } 6) \end{bmatrix}$$

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$$(3) \begin{bmatrix} H_3N \\ H_3N \end{bmatrix} Pt \underbrace{\begin{pmatrix} Cl \\ NH_2(CH_2)_n - H_2N \end{pmatrix}} Pt \underbrace{\begin{pmatrix} Cl \\ NH_3 \end{pmatrix}}$$

- (4) None of the above is correct.
- 172. Select the incorrect statement about metal carbonyls?
  - (1) Metal acts as Lewis base as well as Lewis acid
  - (2) CO acts as Lewis base as well as Lewis acid
  - (3)  $p\pi$ - $p\pi$  back bonding takes place
  - (4)  $p\pi$ - $d\pi$  back bonding takes place
- 173. The following metal carbonyls are given:
  - (I)  $[Mn(CO)_6]^{\oplus}$
  - (II)  $[Cr(CO)_6]$
  - (III)  $[V(CO)_6]^{\odot}$

Which of the following is correct order of CO bond strength in the above complexes

- (1) I > II > III
- (2) III > II > I
- (3) II > I > III
- (4) III > I > II
- 174. The following compounds are given:
  - (I) [Mn(CO)]<sup>⊙</sup>
- (II) CO
- (III) OC  $\rightarrow$  BH<sub>3</sub>
- (IV) [Fe(CO)<sub>5</sub>]

Select the correct CO bond order in the given compounds

- (1) IV > III > I > II
- (2) I > IV > III > II
- (3) II > I > IV > III
- (4) III > II > IV > I
- 175. The  $\pi$ -acid ligand which uses its d-orbital during synergic bonding is its complex compound is:
  - (1) PR<sub>3</sub>

 $(3) C_6 H_6$ 

- (4) NO<sup>⊕</sup>
- 176. Which of the following ligand does not act as  $\pi$ -acid ligand?
  - $(1) O_2^{2-}$

 $(2) C_2 H_4$ 

 $(3) N_{2}$ 

- 177. Select the correct statement about the above given compound
  - (1) 'C—O' bond is weakest in cation and strongest in anion.
  - (2) 'C—O' bond is strongest in cation and weakest in anion.
  - (3) 'C—O' bond is longer in cation than in the anion.
  - (4) ('M—C')  $\pi$ -bonding is higher in the cation
- 178. The  $\pi$ -acid ligand which uses its d-orbital during synergic bonding in its complex compound.
  - (1) NO

(3) PR<sub>3</sub>

(4) CN<sup>⊙</sup>

#### Jahn-Teller Distortion

- 179. Which of the following configuration is more stable for the  $[Cu(NH_3)_A]^{2+}$ .

  - $(1) \ t_{2g}^6 (d_{z^2})^2 (d_{x^2 v^2})^1 \qquad (2) \ t_{2g}^6 (d_{z^2})^1 (d_{x^2 v^2})^2$
  - (3)  $t_{2g}^5 (d_{z^2})^2 (d_{r^2 v^2})^2$  (4) All
- 180. Which of the following configuration high spin octahedral complexes shown strong distortion.
  - (I)  $t_{2\rho}^3 e_{\rho}^1$

- (II)  $t_{2g}^3 e_g^3$
- (III)  $t_{2g}^{0} e_{g}^{0}$
- (IV)  $t_{2g}^{1} e_{g}^{0}$

(1) I, II

(2) I, II, III

(3) II, III

- (4) I, III, IV
- 181. Slow spin octahedral complexes show strong distortion.
  - (I)  $t_{2g}^1 e_g^0$

- (II)  $t_{2g}^3 e_g^0$
- (III)  $t_{2g}^6 e_g^1$
- (IV)  $t_{2g}^6 e_g^3$

(1) I, II

- (2) I, II, III
- (3) III, IV

- (4) I, III, IV
- 182. Which of the following configuration in either high spin or low spin complexes show no distortion.
  - (I)  $t_{2\sigma}^3 e_{\sigma}^2$

- (II)  $t_{2\alpha}^6 e_{\alpha}^2$
- (III)  $t_{2g}^3 e_g^0$
- (IV)  $t_{2g}^6 e_g^1$

(1) I, II

- (2) II, III
- (3) I, II, III
- (4) All
- 183. Which of the following statement is/are correct.
  - (I) Cl has greater trans effect than NH<sub>3</sub>.
  - (II) Trans effect us used in the synthesis of cisplation (cisisomer) and its trans isomer starting from PtCl<sub>4</sub><sup>2-</sup>.
  - (III) Starting from [Pt(NH<sub>3</sub>)<sub>4</sub>]<sup>2+</sup>, the synthesis of cisplatin (cis-isomer) is obtained exclusively.
  - (IV) CH<sub>3</sub> has greater trans effect than H<sup>-</sup>.
  - (1) I, II

(2) II, III

- (3) III, IV
- (4) I, III

### Multiple Correct Answers Type

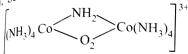
### Naming, Terminology and Ligands

- 1. Select the correct statement(s) for double salt.
  - (1) Double salts are stable in solid state but lose their identity in aqueous solution.
  - (2) In double salt the properties of constituent ions are not changed in their aqueous solution.
  - (3) Double salts are stable in solid state and do not lose their identity in aqueous solution.
  - (4) In double salt the properties of constituent ions are changed in their aqueous solution.
- 2. Which of the following ligand(s) is/are ambidentate?
  - (1)  $NOS^{\Theta}$
- (2) SCN<sup>⊖</sup>

 $(3) NO_2^{\Theta}$ 

- (4) CH<sub>3</sub>COO<sup>⊖</sup>
- 3. Select the correct IUPAC name for  $[CoCl_2(en)_2]_2(ClO_3)_2$ .
  - (1) Dichloridobis (ethylenediamine)cobalt(III) chlorate
  - (2) Dichloridobis (ethane-1, 2-diamine)cobalt(III) chlorate
  - (3) bis {dichloridoethylenediaminecobalt(III)} chlorate (4) bis {di(chlorido)ethylenediaminecobalt(III)} chlorate
- 4. Bidentate ligands are
  - (1)  $C_2O_4^{2-}$  (oxalate)
  - (2) en (ethylenediamine)
  - (3) DMG (dimethyl glyoxime) (4) Gly (glycine)
- 5. Which of the following complex(s) is/are having correct name?

- (I)  $Cs[Pt(NH_3)l_5]$  Ceasium amminepentaiodidoplatinate(IV) (2)  $[Ag(CN)_2]^{\Theta}$  Dicyanidoargentate(I) ion
- $^{(3)}_{(3)}$  Rb<sub>3</sub>[Cr(C<sub>2</sub>O<sub>4</sub>)<sub>3</sub>]-Rubidium trioxalatochromate(III)
- (4) K<sub>2</sub>[Ni(EDTA)] Potassium ethylenediaminetetraacetatoni ckel(II)
- Which can form chelates?
- (1) Ethylene diamine
- (2) Oxalate
- (3) Glycinate
- (4) Cyanide
- , Select the correct IUPAC name for the following:



- (1) Tetramminecobalt inedicobalt (III) ion (III)- $\mu$ -amido- $\mu$ -peroxidotetraamm
- (2) μ-Amido-μ-peroxidobis(tetraammine)dicobalt-(III) ion
- (3) μ-Amido-μ-peroxidobis(tetraamminecobalt(III)) ion
- (4) μ-Amido-μ-peroxidooctaamminedicobalt(III) ion
- & Which of the following statement(s) is/are correct?
- (1) Primary valency of the central metal of a complex is always satisfied by anions.
- (2) Secondary valency of the central metal of a complex may be satisfied by either negative ions or neutral molecules.
- (3) Species which show primary valencies in a complex compound can be precipitated out.
- (4) None of these
- 9. Which of the following complex(s) is/are an example of homoleptic complex?
- $(1) [Co(NH_3)_6]^{3+}$
- $(2) \left[ Cr(H_2O)_6 \right]^{3+}$
- (3)  $[Ni(NH_3)_6]^{2+}$
- (4) [Ni(NH<sub>3</sub>)<sub>4</sub>Cl<sub>2</sub>]
- 10. Which of the following ligand(s) can act as  $\pi$ -acid ligand?
  - (1)  $B_3 N_3 H_6$
- (2)  $\pi$ -cyclopentadienyl
- (3)  $\pi$ -Allyl
- (4) σ-cyclopentadienyl

#### somerism

- 11. Which of the following molecule(s) is/are **not** showing optical isomerism?
  - (1) [Co(NH<sub>3</sub>)<sub>3</sub>1]<sup>⊕</sup>
- (2)  $[Co(en)(NH_3)_2]^{2+}$
- (3)  $[Co(H_2O)_4(en)]^{3+}$
- $(4) \left[ \text{Co(en)}_2 (\text{NH}_3)_2 \right]^{3+}$
- 12. Which of the following complex ion(s) is/are **not** expected to absorb visible light?
  - (1)  $[\text{Ti(en)}_2(\text{NH}_3)_2]^{4+}$
- $(2) \left[ \text{Cr(NH}_3)_6 \right]^{3+}$
- $(3) [Zn(NH_3)_6]^{2+}$
- $(4) [Sc(H_2O)_3(NH_3)_3]^{3+}$
- 13. The complex [Fe(H<sub>2</sub>O)<sub>5</sub>NO]<sup>2+</sup> is formed in the brown ring test for nitrates when freshly prepared FeSO<sub>4</sub> solution is added to aqueous solution of NO<sub>3</sub><sup>⊙</sup> followed by addition of conc. H<sub>2</sub>SO<sub>4</sub>. Select correct statements about this complex:
  - (1) Colour change is due to charge transfer.
  - (2) It has iron in +1 oxidation state and nitrosyl as  $NO^{\oplus}$ .
  - (3) It has magnetic moment of 3.87 BM confirming three unpaired electrons in Fe.
- (4) In complex Fe has d<sup>2</sup>sp<sup>3</sup> hybridisation.

- **14.** Which of the following represent the correct sequence of indicated property?
  - (1)  $Mn^{2+} < Ni^{2+} < Co^{2+} < Fe^{2+}$ : magnetic moment
  - (2) FeO > CoO > NiO: basic character
  - (3) Sc < Ti < Cr < Mn: number of oxidation states
  - (4) 1.73  $\mu$ : one unpaired electron
- 15. Which of the following complexes are diamagnetic?
  - $(1) [Aul_4]^{\Theta}$
- $(2) [Co(H_2O)_6]^{3+}$
- (3)  $[CoI_6]^{3-}$
- (4) [Co(CO)<sub>4</sub>]<sup>⊙</sup>
- **16.** Which of the following molecule(s) is/are showing optical isomerism?
  - $(1) \left[ \text{Co(NH}_3)_3 \text{Br}_3 \right]$
- (2)  $[Co(en)Br_2(NH_3)_2]^{\oplus}$
- (3)  $[Co(en)_3]^{3+}$
- $(4)[Co(en)_2Br_2]^{\oplus}$
- 17. Both geometrical and optical isomerisms are not shown by
  - (1) dibromidobis (ethylenediamine) cobalt(III) ion
  - (2) tetraamminedibromido cobalt(III) ion
  - (3) tetraamminedibromido cobalt(III) ion
  - (4) trioxalatochromate(III) ion
- **18.** Which of the following statement(s) is/are correct?
  - (1) The complexes [Nil<sub>4</sub>]<sup>2-</sup> and [Ni(CN)<sub>4</sub>]<sup>2-</sup> differ in state of hybridisation of nickel.
  - (2) The complexes  $[Nil_4]^{2-}$  and  $[Ni(CN)_4]^{2-}$  differ in geometry.
  - (3) The complexes  $[Nil_4]^{2-}$  and  $[Ni(CN)_4]^{2-}$  differ in the magnetic properties.
  - (4) The complexes [Nil<sub>4</sub>]<sup>2-</sup> and [Ni(CN)<sub>4</sub>]<sup>2-</sup> differ in primary valencies of nickel.
- 19. In which case geometrical isomer cis is possible with M as metal ion if complexes are square planar having CN = 4?
  - $(1) MX_2Y_2$
- (2) MX, Y
- $(3) MXY_2Z$
- $(4) MX_4$
- **20.**  $d_{x^2-y^2}$  orbital is involved in which of the following hybridisation?
  - $(1) sp^3d^3$

 $(2) dsp^2$ 

 $(3) sp^3d^2$ 

- $(4) sp^3 d$
- **21.** Which complex species does/do not exhibit geometrical isomerism and only have two stereoisomerism?
  - (1) [PtBrI(gly)]<sup>©</sup>
- (2) [Cr(EDTA)]
- (3)  $\left[\operatorname{Cr(acac)}_{2}(\operatorname{en})\right]^{\oplus}$
- (4) [Pd(CN)(OX)(gly)]
- **22.** Which of the following complex(s) cannot exhibit both geometrical and optical isomerism?
  - (1)  $[Co(H_2O)Br_3]$
- (2) [Pt Br Cl FI]<sup>-2</sup>
- (3)  $[\text{Fe Cl}_2(\text{en})_2]^{\oplus}$
- (4)  $[Ru(en)_3]^{+3}$
- 23. Select the correct statement about the complex  $[Cr Br(CN)(en)_2]^{\oplus}$ ?
  - (1) It has three optically active isomers: d, l and trans form
  - (2) Only the cis isomer shows optical activity
  - (3) It shows two geometrical isomers *cis* and *trans*.
  - (4) Cis and trans forms are not diastereomers to each other

- 24. Which of the following statement(s) is/are correct?
  - (1) IUPAC name of Ca[Cr(CN)<sub>2</sub>O<sub>2</sub>(O<sub>2</sub>)(H<sub>2</sub>O)] is calcium aquadicyanoperoxosuper oxo chromate (III)
  - (2)  $[\operatorname{Cr} \operatorname{Cl} \operatorname{I} (\operatorname{en})_2]^{\oplus}$  shows optical isomerism
  - (3) [Pt abcd]<sup> $n\pm$ </sup> type and [Pt abcedf]<sup> $n\pm$ </sup> type compounds shows 3 geometrical and 30 stereoisomer's respectively
  - (4) Cis and trans forms are diastereomers to each other
- 25. Which of the following statement is correct for the complex [CrBr<sub>2</sub>(OH)<sub>2</sub>(NH<sub>3</sub>)]<sup>2-</sup> ion?
  - (1) It has three geometrical isomers
  - (2) It shows four stereoisomer's
  - (3) Only one stereoisomer is optically active and remaining are inactive
  - (4) The complex have three unpaired  $e^{-}$ 's
  - 26. In the test for NO<sub>3</sub> ion, the dark brown ring complex is formed, which statement(s) is/are correct of this complex.
    - (1) Fe and No both have +1 charge
    - (2) The colour is due to charge transfer spectra.
    - (3) Fe has +2 oxidation state and NO is neutral
    - (4) The complex can be represented as  $[Fe(H_2O)_4NO]^{+2}$
  - 27. In an aqueous solution of  $NiBr_2$ , if (en) is progressively added in molar ratios such as Ni: en:: 1:1, 1:2, 1:3 then three octahedron complexes x, y, z formed respectively. Select the correct statement(s) about x, y and z.
    - (1) Complex x has maximum value of absorbed wavelength
    - (2) Complex y is coloured
    - (3) Complex z has maximum number of chelates
    - (4) All three are paramagnetic outer orbital complexes
- 28. Which of the following pair of complex compound(s) has/ have different colour?
  - (1) d and l form of  $[Ni(en)_3]^{2+}$
  - (2) cis and trans form of  $[IrCl_2(en)_2]Br$
  - (3)  $[Cr(NO_2)_2(NH_3)_4]^{\oplus}$  and  $[Cr(ONO)_2(NH_3)_4]^{\oplus}$
  - (4) [CrCl(NO<sub>2</sub>)(NH<sub>3</sub>)<sub>4</sub>]Cl and [CrCl<sub>2</sub>(NH<sub>3</sub>)<sub>4</sub>]NO<sub>2</sub>
- **29.** The complex  $[Ni(PPh_3)_2(CNS)_2]$  is paramagnetic. The analogous complex of  $Pd^{+2}$  is diamagnetic. The isomerism shown by  $Pd^{+2}$  complex is/are:
  - (1) Polymerisation
- (2) Linkage
- (3) Optical
- (4) Geometrical
- **30.** Which of the following complex ion(s)/compounds shows geometrical isomerism but none of them shows optical isomerism?
  - (1) [CoCl<sub>4</sub>(en)]<sup>(5)</sup>
- (2) [Pt Br  $I(H_2O)(NH_3)$ ]
- (3)  $[Cr(en)_2]^{3+}$
- (4)  $[CrCl_3(H_2O)_2(NH_3)]$
- **31.** In which of the following compounds *d*-orbitals lose their degeneracy?
  - (1) Anhydrous CuSO<sub>4</sub>
- (2)  $K_3[Fe(CN)_6]$
- (3)  $K_4[Fe(CN)_6]$
- (4) CuSO<sub>4</sub>.5H<sub>2</sub>O

### Hybridisation, VBT, CFT

**32.** A *d*-block element forms octahedral complex, but its spin magnetic moment remains same either in strong field or in weak field ligand. Which of the following is /are correct?

- (1) Element always forms colourless compound.
- (2) Number of electrons in t<sub>2g</sub> orbitals are higher than in e<sub>g</sub> orbitals.
- (3) It can have either  $d^3$  or  $d^8$  configuration.
- (4) It can have either  $d^7$  or  $d^8$  configuration.
- **33.** Which of the following is/are characteristic of a tetrahedral complex?
  - (1)  $d_{y^2-y^2}$  and  $d_{z^2}$  orbitals are low energy orbitals.
  - (2) Most tetrahedral complexes are high spin.
  - (3) Crystal field splitting is found double in octahedral complexes.
  - (4) Splitting pattern in tetrahedral complex is just opposite of that in octahedral complexes.
- **34.** The complex  $K_4[Zn(CN)_4(O_2)_2]$  is oxidised into  $K_2[Zn(CN)_4(O_2)_2]$ , then which of the following is/are correct:
  - (1) Zn(II) is oxidised in to Zn(IV)
  - (2) Paramagnetic moment decreases
  - (3) O—O bond length decreases
  - (4) Paramagnetic moment increases
- 35. Select the correct statement:
  - (1) [Co(H<sub>2</sub>O)<sub>6</sub>]<sup>3+</sup> is Co(III), low spin, 0 unpaired electron, diamagnetic
  - (2)  $[CoF_6]^{3-}$  is Co(III), high spin  $d^6$ , 4 unpaired electron, paramagnetic
  - (3)  $[RhF_6]^{3-}$  is Rh(III), low spin  $d^6$ , 0 unpaired electrons diamagnetic
  - (4)  $[Fe(CN)_6]^4$  is high spin  $d^6$ , 0 unpaired electron diamagnetic
- **36.**  $[Co(H_2O)_6]^{3+}$  complex is
  - (1) High spin complex
  - (2) Having  $d^2sp^3$ -hybridization
  - (3) Low spin complex
  - (4) Having octahedral structure
- 37. Colourless, tetrahedral complexes among the following are
  - (1) K<sub>3</sub>[Cu(CN)<sub>4</sub>]

(2) Ca[NiCl<sub>1</sub>]

 $(3) \text{Na}[BF_4]$ 

- (4) Ni(CO),
- **38.** In which of the following complex ion five atoms are lying in a line including metal?
  - $(1) [Ag(CN)_2]^{\odot}$
- (2)  $[Pt(CN)_4]^{2-}$
- $(3) [Ag(SCN)_2]^{\odot}$
- (4)  $[Zn(CN)_4]^2$
- **39.** Select the correct statement(s) for given carbonyl compounds:
  - (1) "CO" bond order is lesser in [Nb(CO)<sub>6</sub>]<sup>©</sup>
    Then in [Tc(CO)<sub>6</sub>]<sup>⊕</sup>
  - (2) "Nb—C" bond order in [Nb(CO)<sub>6</sub>]<sup>⊕</sup> is greater than "Tc—C" bond order in [Tc(CO)<sub>6</sub>]<sup>⊕</sup>
  - (3) [Tc(CO)<sub>6</sub>]<sup>⊕</sup> acts as reducing agent and [Nb(CO)<sub>6</sub>]<sup>⊕</sup> acts as oxidising agent.
  - (4) [Nb(CO)<sub>6</sub>]<sup>©</sup> acts as reducing agent and [Tc(CO)<sub>6</sub>]<sup>⊕</sup> acts as oxidising agent.

Select the correct statement(s):

- (1) In  $dsp^2$  hybridisation,  $d_{z^2}$  orbital of central metal atom/ ion is used.
- $_{(2)}$  Facial and meridional isomers associated with  $[Ma^3b^3]^{n\pm}$ type complex compounds, both are optically inactive.
- (3) In metal carbonyl C—O increases compared to that CO molecule.
- (4) Chelation effect is maximum for five and six membered rings.

11. Select the correct statements:

- (1) Compounds [Cr(H<sub>2</sub>O)<sub>6</sub>]Br<sub>3</sub> and [CrBr<sub>3</sub>(H<sub>2</sub>O)<sub>3</sub>].3H<sub>2</sub>O are hydrate isomers.
- (2) Greater the charge on the central metal cation, greater the value of  $\Delta(CFSE)$
- (3)  $[CrBr_2(NH_3)_2(en)]^{\oplus}$  complex ion will have four different
- (4) In the complex ion  $[CoF_6]^{3-}$ ,  $F^{\odot}$  is a weak ligand, so that  $\Delta_0$  < P and it is low spin complex.
- 12. Select the correct statement(s):
  - (1) Ni(CO)<sub>4</sub> is low spin complex
  - (2)  $[FeF_6]^{3-}$  is high spin complex
  - (3) Strong ligand like  $\mathrm{CN}^{\odot}$  and  $\mathrm{NO_2}^{\odot}$  generally form low spin complexes.
  - (4) Weak ligands  $F^{\ominus}$ ,  $Cl^{\ominus}$  and  $OH^{\ominus}$  usually form high spin complexes.
- 43. Select the correct statement(s): for octahedral complexes:
  - (1) In octahedral complexes, its magnetic moment remains same either in strong field or in weak field ligand in d<sup>9</sup> configuration.
  - (2) Number of  $e^{-1}$ 's in  $t_{2\sigma}$  orbitals are higher than in  $e_{\sigma}$  orbitals.
  - (3)  $d^3$  and  $d^8$  configuration cannot exist in both high spin and low spin forms.
  - (4) Chelating ligands are at least bidentate ligands.
- 44. Select the correct stability order for the following complexes.
  - (1)  $[Cu (trien)]^{2+} > [Cu (en)_2]^{2+} > [Cu (NH_3)_4]^{2+}$
  - (2)  $[Ir(H_2O)_6]^{3+} > [Rh(H_2O)_6]^{3+} > [Co(H_2O)_6]^{3+}$
  - (3)  $[Cr(NH_3)_6]^{3+} > [Cr(NH_3)_6]^{2+} > [Cr(NH_3)_6]^{\oplus}$
  - (4)  $[\text{Fe (NH}_3)_6]^{3+} > [\text{Fe (NO}_2)_6]^{3-} > [\text{Fe (H}_2\text{O})_6]^{3+}$
- 45. Select the correct statement(s):
  - (1) Order of energies of d-orbitals of metal ion in a square planar complex is:

- $d_x^2 y^2 > d_{xy} > d_z^2 > d_{zx} = d_{yz}$ (2) The CFSE of [Co(NH<sub>3</sub>)<sub>6</sub>]Br<sub>3</sub> is -2.4 $\Delta_0$ .
- (3) The magnitude of CFSE in octahedral field depends on nature of the ligand.
- (4) When  $NH_3$  is added to  $[Ni(H_2O)_6]^{2+}$ , its magnetic moment does not charge.
- 46. Select the correct statement(s)
  - (1) Stability order of complexes is  $[Cr(OX)_3]^{3-} > [Cr(H_2O)_6]^{3+} > [Co(ONO)_6]^{3-} > [CoF_6]^{3-}$
  - (2) Among  $d^4$ ,  $d^5$ ,  $d^6$  and  $d^7$  configuration for an octahedral complexes, the maximum CFSE is given by low spin with  $d^5$  configuration.

- (3) In an octahedral field, the  $t_{2g}$  orbitals are raised in energy by  $0.4\Delta_0$ .
- (4) Stability of complex is:  $[Ni (en)_2]^{2+} > [Ni (DMG)_2]$

### **Application of Coordination Compounds**

- 47. The coordination number of a central metal atom in a complex(s) is/are not determined by:
  - (1) The number of only anionic ligands bonded to the metal
  - (2) The number of ligands around metal ion bonded by  $\pi$ -bonds.
  - (3) The number of ligands around a metal ion bonded by both  $\pi$  and  $\sigma$ -bonds.
  - (4) The number of ligands around a metal ion bonded by σ-bonds.
- **48.** Which of the following statement(s) is/are incorrect?
  - (1) Metal carbonyls are the examples of only  $\sigma$ -bonded organometallic complexes.
  - (2) Metal carbonyls are the examples of only  $\pi$ -bonded organometallic complexes.
  - (3) Metal carbonyls are the examples of organometallic complexes which involve both  $\sigma$  and  $\pi$ -bonds between metal and carbon of the carbonyl group.
  - (4) Metal carbonyls involve both  $\sigma$  and  $\pi$ -bonds between metal and oxygen of the carbonyl group.
- **49.** Which of the following is an example of  $\pi$ -bonded organometallic complex?
  - (1) Ferrocene
- (2) Dibenzenechromium
- $(3) Zn(C_2H_5)_2$
- $(4) Pb(C_2H_5)_4$
- 50. Which of the following is/are example(s) of σ-bonded organometallic compound?
  - $(1) Al_2(CH_3)_6$
- (2)  $Pb(CH_3)_4$
- $(3) Zn(C_2H_5)_2$
- (4) Ferrocene
- 51. Which of the following statement is correct regarding metal carbonyl?
  - (1) In  $Mn_2(CO)_{10}$ , bond order of Mn—Mn is 0.
  - (2) In Fe<sub>2</sub>(CO)<sub>9</sub>, number of Fe—Fe bonds is 1.
  - (3) In Ni(CO)<sub>4</sub>, all bond length are same.
  - (4) Fe(CO)<sub>5</sub> is diamagnetic.
- **52.** Select correct statements:
  - (1)  $[Ni(en)_3]^{2+}$  is less stable than  $[Ni(NH_3)_6]^{2+}$ .
  - (2) Increase in stability of the complexes due to the presence of multidentate cyclic ligand is called macro-cyclic effect.
  - (3)  $[Ni(en)_3]^{2+}$  is more stable than  $[Ni(NH_3)_6]^{2+}$ .
  - (4) For a given ion and ligand, the greater the charge on the metal ion, the greater is the stability.
- 53. In which of the following cases, the synergic bonding takes place at the  $\pi$ -orbital of the ligand?
  - $(1) \left[ \text{PtCl}_3(\text{C}_2\text{H}_4) \right]^{\odot}$
- (2)  $[Ni(PF_3)_4]$
- (3)  $Cr(C_6H_6)_2$
- (4)  $[Fe(\pi-C_5H_5)_2]$

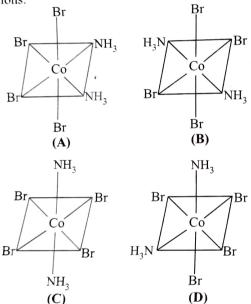
- 54. Which of the following statement(s) is/are correct?
  - (1) The stability constant of  $[Co(H_2O)_6]^{3+}$  is larger than that of  $[Co(H_2O)_6]^{2+}$ .
  - (2) The cyano complexes are more stable than those formed by halide ions.
  - (3) The stability of halide complexes follows the order  $I^{\Theta} > Br^{\Theta} > Cl^{\Theta} > F^{\Theta}$
  - (4) The stability constant of  $[Cu(NH_3)_4]^{2+}$  is less than that of  $[CuCl_{A}]^{2-}$ .

### **Linked Comprehension Type**



Paragraph 1

Consider the following isomers of  $[Co(NH_3)_2Br_4]^{\Theta}$  and answer the questions:



- 1. Select the correct statement:
  - (1) Pairs of A and D are same and pairs of B and C are also same.
  - (2) All have chiral centres.
  - (3) A and C are enantiomers.
  - (4) B and D are enantiomers.
- 2. Out of these isomers:
  - (1) A and D are trans and B and C are cis
  - (2) A and D are cis and B and C are trans
  - (3) A and B are cis and C and D are trans
  - (4) A and B are trans and C and D are cis
- 3. In the complex [Zn PORS]<sup>2+</sup>:
  - (1) There is chirality
  - (2) There is geometrical isomerism
  - (3) Both (a) and (b)
  - (4) None of these
- 4. If PQRS are four different ligands, then how many geometric isomers will be found for square planar [Pt PQRS]<sup>2+</sup>?
  - (1) 1

(2)2

(3)3

(4)4

### Paragraph 2

Ligands are broadly classified into two types, classical and nonclassical ligands depending on their donor and acceptor ability. Classical ligands form classical complexes while non-classical ligands form non-classical complexes. Bonding mechanism in non-classical is called synergic bonding.

5. In compound  $[M(Co)_n]^z$ , the correct match for highest 'M-C' bond length for given M, n and z respectively

	M	n	Z
(1)	Ti	6	-2
(2)	Mn	6	+1
(3)	Cr	6	0
(4)	V	6	-1

- 6. Synergic bonding is absent in:
  - (1)  $[Ni(CN)_{4}]^{4}$
- (2)  $[Cr(CO)_3(B_3N_3H_6)]$
- (3) [Mo(Co)<sub>6</sub>]
- (4) [Sc(Co)<sub>c</sub>]<sup>3+</sup>
- 7. Which is not  $\pi$ -acceptor ligand?
  - $(1) \sigma \overset{\odot}{C_5} H_5$
  - (2) PH<sub>3</sub>

  - $(4) B_3 N_3 H_6$

### Paragraph 3

Bond lengths and vibrational spectra are the two important physical evidences supporting the synergic bonding in nonclassical complexes. Vibrational spectra is based on the fact that the compression and extension of a bond may be analogous to the behaviour of a spring and obeys Hook's law:

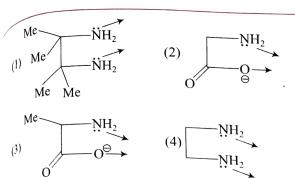
- 8. In [Mn<sub>2</sub>(CO)<sub>10</sub>] carbonyl complex, which d-orbitals of Mn-atom is not involved in synergic bonding between Mn and CO ligand.
  - $(1) d_{xy}$

(3)  $d_{2x}$ 

- (2)  $d_{yz}$ (4) None of these.
- 9. In which of the following complex stretching frequency for CO ligand is least and bond energy of 'M - C' bond is highest.
  - (1)  $[Mo(CO)_3 (PR_3)_3]$
- (2) [Mo(CO)<sub>3</sub> (dien)]
- (3)  $[Mo(CO)_3(PF_3)_3]$
- (4) [Mo(CO)<sub>3</sub> (PCl<sub>3</sub>)<sub>3</sub>]
- 10. In which of the following ligand,  $\sigma$ -bond strength does not change during synergic bonding in their respective complexes.
  - $(1) P(C_2H_5)_3$
- $(2) N_{2}$
- $(3) CH_2 = CH_2$
- (4) CO

VBT and CFT play very important role in determining the geometry of complex compound/ion and electronic distribution of d-orbitals of central metal atom/ion in presence of given ligands respectively. A very important property of complex compound/ ion is to display isomerism.

11. Which of the ligand can show geometrical as well as optical isomerism in square planar homoleptic complex?



Which of the following complex compound(s) is/are inner orbital complex as well as low spin complex ion(s)?

- (1)  $[Ni(CN)_6]^{4-}$
- (2)  $[Ag(S_2O_3)_2]^{3-}$
- $(3) \left[ \text{Cu(NH}_3)_4 \right]^{2+}$
- (4)  $[IrF_{-}]^{3-}$
- Which of the following compound(s) shows at least two types of structural isomerism.
  - (1)  $Na[Fe(CN)_2(H_2O)_4]$
- (2)  $[Co(SCN)(H_2O)_5]Cl_2$
- (3)  $[PdCl(NO_2)(NH_3)_4]SO_4$  (4)  $[Cr(NH_3)_6][Co(NO_2)_6]$
- In which of the following complex transition of electron occurs from one shell to other shell of central metal.
- (1)  $[Co(H_2O)_6]^{2+}$
- $(2) [Ni(CN)_6]^{4-}$
- $(3) [Rh(NH_3)_6]^{2+}$
- (4) [Fe(H<sub>2</sub>O)<sub>5</sub>NO]<sup>2+</sup>
- 5. Which of following hydrated complex ion has high intensity colour in aqueous solution.
- (1)  $[Co(H_2O)_6]^{2+}$
- (2)  $[Mn(H_2O)_6]^{3+}$
- (3)  $[Mn(H_2O)_6]^{2+}$
- (4)  $[Ni(H_2O)_6]^{2+}$

#### Paragraph 5

valence bond theory describes the bonding in complexes in terms fcoordinate-covalent bonds resulting from overlap filled ligand orbitals with vacant metal hybrid orbitals. This theory explains magnetic behaviour and geometrical shape of coordination ompounds. Magnetic moment of a complex, compound can be letermined experimentally and theoretically by using spin only

Magnetic moment  $\sqrt{n(n+2)}$  BM (where n = No. unpairedelectrons).

- 6. The value of spin only magnetic moment for octahedral complex of the following configuration is 2.84 BM. The correct statement is
  - (1) d<sup>4</sup> (in weak field ligand)
  - (2)  $d^2$  (in weak field and in strong field ligand)
  - (3)  $d^3$  (in weak field and in strong field ligand)
  - (4) d<sup>5</sup> (in strong field ligand)
- 17. Ni<sup>2+</sup> cation combines with a uninegative monodentate ligand  $X^{\Theta}$  to form a paramagnetic complex  $[NiCl_4]^{2-}$ . The number of unpaired electron(s) in central metal cation and geometry of this complex respectively are
  - (1) One, tetrahedral
- (2) Two, tetrahedral
- (3) One, square planar
- (4) Two, square planar

### <sup>Para</sup>graph 6

 $\S_{\text{quare planar complexes are formed by } d^8 \text{ ions with strong field}$  $_{\rm igands}$ . The crystal field splitting  $\Delta_0$  is larger for the second and third row transition elements and for more highly charged species. All the complexes having  $4d^8$  and  $5d^8$  configurations are mostly square planar including those with weak field ligands such as halide ions. Square planar complexes can show geometrical isomerism but they do not show optical isomerism due to the presence of plane of symmetry.

- 18. Which of the following molecule has synergic bonding?
  - (1)  $[Fe(\pi-C_5H_5)_2]$
- $(2) [RhCl (PPh_3)_3]^{3+}$
- (3)  $[Fe(Phen)_{2}]^{3}$
- (4) All are having synergic bonding
- 19. Among the following complexes, which has a square planar geometry?
  - (1)  $[RhCl(CO)(PPh_3)_2]$
- $(2) K_3[Cu(CN)_4]$
- $(3) [Ni(CO)_4]$
- $(4) K_{2}[Zn(CN)_{4}]$
- 20. Which of the following complex is low spin?
  - (1) All are low spin complexes
  - (2) [Ni(CO)<sub>4</sub>]
  - (3)  $[Pt(NH_3)_4]^{2+}$
  - $(4) [Ni(NH_2)_6]^{2+}$

#### Paragraph 7

If in the mixed carbonyl, the other ligand is also  $\pi$  acceptor, it would compete with the ligand CO for gaining the metal  $d_{\pi}$  electron charge. The higher is the extent of back donation in CO, the lesser will be the stretching vibration frequency for C—O bond. If  $PP_3$  is better  $\pi$ -acceptor than CO, then answer the following.

- 21. Select the correct order of M—C bond order in the following molecule and ions:
  - I. [Ni(CO)<sub>4</sub>]
- II. [Co(CO),]<sup>⊙</sup>
- III.  $[Fe(CO)_4]^{2-}$
- (1) I > II > III
- (2)I = II = III
- (3) II > III > I
- (4)I < II < III
- 22. Select the correct order of stretching vibration frequency C—O bond in following molecules:
  - I.  $[Ni(CO)_{a}]$
- II. [Ni(PF<sub>3</sub>)(CO)<sub>3</sub>]

(1) I > II

(2)I < II

(3) I = II

- (4) cannot be predicted
- 23. Select the correct order of C—O bond length in the following
  - I.  $[Mo(CO)_3 (PF_3)_3]$ **III.**  $[Mo(CO)_3(P(Me)_3)_3]$ 
    - II. [Mo(CO)<sub>3</sub> (PCl<sub>3</sub>)<sub>3</sub>]
  - (1) I > II > III
- (2) III > I > II
- (3) II > III > I
- $(4)\,\mathrm{I}<\mathrm{II}<\mathrm{III}$

### Paragraph 8

Most of the metal carbonyls obey inert gas rule which states that the compounds in which the central metal atom appears to have attained the configuration of a noble gas either by the sharing or by the transfer of electrons tend to be more stable.

- **24.** Which of the following has lowest C—O bond order?
- (1)  $[Mn(CO)_6]^{\oplus}$
- (2) [Co(CO)<sub>4</sub>]<sup>©</sup>
- (3)  $[Fe(CO)_4]^{2-}$
- (4) [Ni(CO)<sub>4</sub>]
- 25. Select the correct order of C—O bond length of the

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- **I.**  $[M(CO)_3(PF_3)]$  **II.**  $[M(CO)_3(PCl_3)]$  **III.**  $[M(CO)_3(PMe_3)]$
- (1) 1 < 11 < 111
- (2) 1 > 11 > 111
- (3) I = II = III
- (4) I = II > III
- 26. Which of the following has highest C-O bond length?
  - (1)  $[Mn(CO)_6]^{\oplus}$
- $(2) \left[ \text{Co(CO)}_{4} \right]^{\Theta}$
- (3)  $[Fe(CO)_4]^2$
- (4)  $[Ni(CO)_4]$

### Paragraph 9

In the manufacture of iron, a gas (A) is formed in the zone of combustion of the blast furnace. The gas (A) reacted with coke in the zone of fusion to form another gas (B). X moles of (B) reacts with iron at 200°C and 100 atm pressure to form a compound (C).

- 27. The d orbital(s) involved in the formation of the complex (C) will be:
  - $(1) d_{-2}$

- (2)  $d_{xy}$  and  $d_{x^2-y^2}$
- $(3) d_{12,12}$  and  $d_{22}$
- $(4) d_{y^2-y^2}$
- 28. The magnetic moment and effective atomic number of the C. respectively, are
  - (1) 4.93 and 36
- (2) 0 and 34
- (3) 0 and 36
- (4) None

#### Paragraph 10

The  $\pi$  acceptor ligands are those which possess vacant  $\pi$ -orbitals in addition to the lone pairs of electrons.

- 29. Which of the following complex ion has lowest M—C bond length?
  - (1) [V(CO)<sub>6</sub>]<sup>Θ</sup>
- (2)  $[Mn(CO)_6]^{\oplus}$
- (3) Ni(CO)<sub>4</sub>
- (4) Fe(CO)<sub>5</sub>
- 30. Which of the following complex ion has the highest C—O bond length?
  - $(1) [V(CO)_{\epsilon}]^{\Theta}$
- (3) Fe(CO)<sub>5</sub>
- (2) Ni(CO)<sub>4</sub> (4) [Mn(CO)<sub>6</sub>]<sup>⊕</sup>
- 31. Which of the following complex/ion has lowest C—O bond order?
  - (1) [V(CO)<sub>6</sub>]<sup>Θ</sup>
- (3) Fe(CO)<sub>5</sub>
- (2) Ni(CO)<sub>4</sub> · (4) [Mn(CO)<sub>6</sub>]<sup>⊕</sup>
- 32. Which of the following complex/ion has lowest M—C bond order?
  - $(1)[V(CO)_i]^{\Theta}$
- (3) Fe(CO),
- (2) Ni(CO)<sub>4</sub> (4) [Mn(CO)<sub>6</sub>]<sup>⊕</sup>

### Paragraph 11

The  $\pi$  acid ligands donate their lone pairs to the metal to form a normal  $\sigma$  bond with the latter in addition to it, the vacant orbitals accept electrons from the filled metal orbitals to form a type of  $\pi$ -bond which suppliments the  $\sigma$  bond.

- 33. Which of the following has lowest M—C bond length?
  - (1)  $[Ni(CO)_4]$
- (2) [Mn(CO)<sub>6</sub>]<sup>⊕</sup>
- (3)  $[Fe(CO)_{4}]^{2-}$
- $(4) [Co(CO)_4]^{\odot}$
- **34.** Which of the following has lowest M—C bond order?
  - (1)  $[Fe(CO)_4]^{2-}$
- $(2) \left[ \text{Co(CO)}_{4} \right]^{\Theta}$
- (3)  $[Ni(CO)_4]$
- $(4)[Mn(CO)_6]^{\oplus}$

- 35. Which of the following has lowest C—O bond length?
  - (1)  $[Fe(CO)_{4}]^{2-}$
- (2)[Co(CO)<sub>4</sub>]<sup>©</sup>
- (3)  $[Ni(CO)_4]$
- (4) [Mn(CO)<sub>6</sub>]<sup>⊕</sup>

### Paragraph 12

Coordination compound plays many important roles in animals and plants. They are essential in the storage and transport of oxygen, as electrons transfer agents, as catalysts, and in photosynthesis. Wide range of application in daily life takes place through formation of complexes. Photographic fixing, qualitative and quantitative analysis, purification of water, metallurgical extraction are some specific worth mentioning.

- 36. The complex [Fe(H<sub>2</sub>O)<sub>5</sub>NO]<sup>2+</sup> is formed in the brown ring test for nitrates when freshly prepared FeSO<sub>4</sub> solution is added to aqueous solution of NO<sub>3</sub> followed by addition of conc. H<sub>2</sub>SO<sub>4</sub>. Select correct statement about this complex:
  - (1) Colour change is due to charge transfer
  - (2) It has iron in +1 oxidation state and nitrosyl as  $NO^{\oplus}$
  - (3) It has magnetic moment of 3.87 BM confirming three unpaired electrons in Fe
  - (4) All the above are correct statements
- 37. Extraction of Ag from sulphide ore and removal of unreacted silver from photographic plate involve complexes:
  - (1)  $[Ag(S_2O_3)_2]^{3-}$  in both
  - (2)  $[Ag(CN)_2]^{\Theta}$  in both
  - (3)  $[Ag(S_2O_3)_2]^{3-}$ ,  $[Ag(CN)_2]^{\Theta}$ (4)  $[Ag(CN)_2]^{\Theta}$ ,  $[Ag_2(S_2O_3)_2]^{3-}$
- 38. Lead poisoning in the body can be removed by
  - (1) EDTA in the form of calcium dthydrogen salt
  - (2) Cis-platin
- (3) Zeisse's salt

- (4) DMG
- 39. Cu<sup>2+</sup> and Cd<sup>2+</sup> both are precipitated as sulphides on passing H<sub>2</sub>S gas in dil. HCl medium. However, precipitation of Cu<sup>2</sup> is prevented by
  - (1) Adding excess of K<sub>4</sub>[Fe(CN)<sub>6</sub>] when Cd<sup>2-</sup> is only
  - (2) Adding excess of KCN when Cu2+ forms stable complex [Cu(CN)<sub>4</sub>]<sup>3-</sup> and Cd<sup>2+</sup> forms unstable complex
  - (3) Adding KCNS when Cu<sup>2+</sup> forms complex [Cu(CNS)<sub>4</sub>]<sup>2</sup> while Cd<sup>2+</sup> does not form complex
  - (4) All of the above
- 40. Arrange the following in order of decreasing number of unpaired electrons:

I.  $[Fe(H_2O)_6]^{2+}$ 

II.  $[Fe(CN)_{o}]^{3-}$ IV. [Fe(H,O),]3+

III.  $[Fe(CN)_6]^4$ 

(2)1, II, III, IV

(1) IV, I, II, III (3) III, II, I, IV

(4) II, III, I, IV

Complex compound with empirical formula Co5NH<sub>2</sub>·NO<sub>2</sub>·Br<sub>2</sub> exist in two isomers A (red) and B (yellow) 1 mole of each A and B gives 2 moles of AgBr when treated with excess of AgNO<sub>3</sub>.

A and B both can show. (1) Jonisation isomerism

(2) Linkage isomerism

(i) Geometrical isomerism

(4) Both (A) & (B)

Correct statement for A & B is: Both A and B contain ONO as ligand

(1) Poor as ligand.

(3) A contains ONO while B contains NO<sub>2</sub> as ligand.

(4) Both A and B contains NO<sub>2</sub> as ligands.

Correct statement for A & B is:

(1) A and B both are paramagnetic

(2) A and B both are diamagnetic

(3) A is paramagnetic while B is diamagnetic

(4) A is diamagnetic while B is paramagnetic

### Natrix Match Type

his section contains questions each with two columns I and II. thich the items given in column I with that in column II.

Column I		Column II	
a.	$[PtCl_3(C_2H_4)]^{\odot}$	p.	Follow EAN
b.	[Co(CO) <sub>4</sub> ] <sup>⊙</sup>	q.	Complex involved in synergic bonding
c.	[V(CO) <sub>6</sub> ] <sup>⊙</sup>	r.	Complex having highest bond length of Co ligand
d.	[Fe(CN) <sub>5</sub> C(CO)] <sup>-3</sup>	s.	Complex having lowest bond length of Co ligand.

2. Match the complexes (in column I) with the type of isomerism (in column II).

	Column I		Column II
a.	[Cr(NH <sub>3</sub> ) <sub>4</sub> Cl <sub>2</sub> ]	p.	Optical
b.	cis[Cr(en) <sub>2</sub> Cl <sub>2</sub> ]	q.	Ionisation
c.	[Cr(en) <sub>2</sub> (NO <sub>2</sub> )Cl] SCN	r.	Coordination
d.	$[Cr(NH_3)_6][Co(CN)_6]$	s.	Geometrical

	Column I		Column II
a.	$[\operatorname{Cr}(\pi\text{-}\operatorname{C}_6\operatorname{H}_6)(\operatorname{NO})_3]$	p.	Coordination number of central metal is six.
b.	$[\operatorname{Cr}(\operatorname{C_2H_4})(\operatorname{CO})_5]$	q.	Bond order of all ligand decreases
c.	$\left[\text{Pt(NO}_2)_2(en)_2\right]^{2+}$	r.	Stable according to EAN rule
d.	Ir(SCN)(SO <sub>4</sub> )(NH <sub>3</sub> ) <sub>4</sub>	s.	Bond order of all M — L bond > 1.0
		t.	Ligands acts as ambidentate

### 4. Match the column.

	Column I		Column II
a.	Two unpaired electron	p.	[Ni(en) <sub>3</sub> ] <sup>2+</sup>
b.	No unpaired electron	q.	
c.	Optical isomerism	r.	[NiCl <sub>2</sub> (SCN) <sub>4</sub> ] <sup>4</sup>
d.	Inner orbital complex	_	[Fe(CN) <sub>6</sub> ] <sup>4</sup>

### 5. Match the column.

Column I		Column II		
a.	$[\mathrm{Cr}(\mathrm{H_2O})_5\mathrm{Br}]^{2+}$	p.	Paramagnetic	
b.	[Cu(en)Cl <sub>4</sub> ] <sup>2-</sup>	q.	Shows geometrical isomerism	
c.	$[Pt(OX)_2]^{2-}$	r.	Shows optical isomerism	
d.	[Fe(OH) <sub>4</sub> ] <sup>⊖</sup>	s.	Do not follow EAN rule	
		t.	Complex having symmetrical bidentate ligand	

#### 6. Match the column.

	Column I		Column II (Number of unpaired electrons)
a.	$[Fe(NH_3)_6]^{2+}$	p.	0
b.	$[MnO_4]^{\Theta}$	q.	5
c.	$[Mn(NH_3)_6]^{2+}$	r.	1
		S.	4

### 7. Math the column.

Column I (Complex ion)			Column II (Property which is different in given pair)
a.	$K_4[Ni(CN)_4]$ and $[Ni(en)_3]S_2O_3$	p.	Number of unpaired electrons
b.	$K_4[NiF_6]$ and $K_2[NiF_6]$	q.	Magnetic behaviour
c.	$K_4[Co(NO_2)_6]$ and $[Fe(H_2O)_6]Cl_3$	r.	Hybridisation
	Sin de la	s.	Geometry

### 8. Match the complex (in column I) with the geometry (in column II).

Column I (Complex ion)		Column II (Value charge on complex ion)	
a.	[Ni(dmg) <sub>2</sub> ]	p.	Tetrahedral
b.	$[ZnCl_4]^2$	q.	Trigonal bipyramidal
c.	$[Co(NO_2)_6]^4$	r.	Square planar
d.	[Fe(CO) <sub>5</sub> ]	s.	Square pyramidal
		t.	Octahedral

### 9. Match the column

	Column I		Column II
a.	Brown ring complex	p.	Octahedral
b.	Calcium nitroprusside	q.	$\mu_{MM} = 0BM$
c.	Ca <sub>2</sub> [Fe(CN) <sub>6</sub> ]	r.	$\mu_{MM} = \sqrt{15} \text{ BM}$
d.	Complex of Ag formed during its extraction	s.	NO <sup>⊕</sup> ligand

#### 10. Match the column.

Column I (Type of complex)		Column II (The change in number of stereoisomer by the associated process with the given complex)	
a.	$[\mathrm{Ma}_2\mathrm{b}_2\mathrm{c}_2]^{n\pm} \xrightarrow{-b/+d} \rightarrow$	p.	6
b.	$[M(AB)_2ab]^{n\pm} \xrightarrow{-a/+b}$	q.	2
c.	$[M(AA)_2 a_2]^{n\pm} \xrightarrow{-a/+c}$	r.	5
d.	$[M(AB)a_3b]^{n\pm} \xrightarrow{-a/+b}$	s.	3
		t.	0

#### 11. Match the column.

Column I			Column II		
a.	[Ma <sub>3</sub> bcd] <sup>n±</sup>	p.	Four optically active isomer		
b.	$[M(AA)b_2cd]^{n\pm}$	q.	Four geometrical isomer		
c.	$[M(AB)_3]^{n\pm}$	r.	All geometrical isomers are optically active		
d.	$[M(AB)b_2c_2]^{n\pm}$	s.	Two pair of enantiomer		
		t.	Two optically inactive isomer		

Note: AA, BB, a, b, c, d are not having chiral centre.

### 12. Match the column.

	Column I		Column II		
a.	[M(AA)b <sub>2</sub> cd]	p.	Complex molecule which shows optical isomerism		
b.	$[M(AAA)b_2c_2]$	q.	Only one cis and one trans isomer		
c.	$[M(AA)_2b_2]$	r.	Only one cis and two trans isomers		
d.	$[M(AA)_3]$	s.	Four geometrical isomers		
		t.	Complex in which any cis isomer is optical active		

### 13. Match the column.

Column I			Column II
a.	[Ma <sub>4</sub> bc]	p.	Six cis isomers
b.	$[\mathrm{Ma}_2\mathrm{b}_2\mathrm{c}_2]$	q.	Four trans isomers

c.	[Ma <sub>2</sub> bcde]	r.	Octahedral complex compound
d.	[Ma <sub>2</sub> b <sub>2</sub> cd]	s.	Four geometrical isomers
		t.	Only two geometrical isomer

### 14. Match the column.

Column I		Column II	
a.	$[M(AB)_3]$	p.	Zero pair of enantiomers
b.	[M(AB)(CD)ef]	q.	Ten pair of enantiomers
c.	[Ma <sub>4</sub> bc]	r.	Four number of stereoisomers
d.	[Ma <sub>3</sub> b <sub>2</sub> c]	s.	Four geometrical isomers

### 15. Match the column.

Column I			Column II		
a.	[Ma <sub>3</sub> bcd]	p.	The number of stereoisomers is two		
b.	$[Ma_3b_3]$	q.	The number of pair of enantiomer is zero		
c.	[Mabcdef]	r.	The number of stereoisomers is five		
d.	$[\mathrm{Ma}_2\mathrm{b}_2\mathrm{c}_2]$	S.	The pair of enantiomer is one		
		t.	The pair of enantiomer is fifteen		

### 16. Match the column.

Column I			Column II
a.	Hexachloridop- latinate(2–)	p.	Monodentate ligand is present in complex/ion
b.	Sodium diammi netetrabromidoc obaltate(III)	q.	Negative ligand is present in complex ion or molecule
c.	Tris (ethylenediamine)copper(II)	r.	Neutral ligand is present in complex ion/molecule sulphate
d.	Hexacarbonyl- manganese hypobromate	s.	Central atom of complex or ion is a member of 3d transition series.
		t.	Octahedral structure of complex ion/molecule

### 17. Match the column.

	Column I		Column II
a.	[Fe(CN) <sub>6</sub> ] <sup>3-</sup>	p.	Optical isomerism
b.	$[Cr(en)_2Cl_2]^{\oplus}$	q.	$d^2sp^3$ -hybridisation
c.	$\left[Ni(NH_3)_6\right]^{2+}$	r.	$d^2sp^3$ hybridisation
d.	$[CoF_6]^{3-}$	s.	$sp^3d^2$ -hybridisation

Match the column.

	Column I		Column II
a.	[Ptl <sub>2</sub> (en)]	p.	Square planar complex
b.	[Pt(NH <sub>3</sub> ) <sub>2</sub> l <sub>2</sub> ]	q.	central atom is a member of 3d transition series
c.	[Pt(NH <sub>3</sub> )(NO <sub>2</sub> )(py) NH <sub>2</sub> OH]	r.	Complex which shows geometrical isomerism
d.	$[Zn(gly)_2]$	s.	Non-planar complex
		t.	Both neutral as well as nega- tive ligand are present in com- plex

19. Match the column.

	Column I		Column II			
a.	[Cr(en) <sub>2</sub> I <sub>2</sub> ] <sup>⊕</sup>	p.	Complex molecule/ion in which neutral ligand is present			
b.	$[Pt(NH_3)_2I_4]$	q.	Complex which shows geometrical isomerism			
c.	[Cr(en) <sub>3</sub> ] <sup>3+</sup>	r.	d <sup>2</sup> sp <sup>3</sup> -hybridisation is present in central atom of complex molecule/ion			
d.	[Cr(gly) <sub>3</sub> ]	s.	Two geometrical isomers			
7		t.	Complex in which only nitrogen atom acts as donor atom			

20. Match the column.

	Column I	Column II		
a.	$[Co(NH_3)_6]^{3+}$	p.	d <sup>2</sup> sp <sup>3</sup> -hybridisation	
b.	Fe <sub>4</sub> [Fe(CN) <sub>6</sub> ] <sub>3</sub>	q.	Octahedral geometry	

	K <sub>3</sub> [Fe(CN) <sub>6</sub> ]	r.	Blue colour due to charge transfer
d.	K <sub>4</sub> [Fe(CN) <sub>6</sub> ]	S.	Six electrons are present in $t_{2g}$ orbitals
		t.	EAN is 36

21. Match the column.

Column I			Column II		
a.	$\left[\operatorname{Cr}(\operatorname{CN})_3(\operatorname{NO}_2)_3\right]^4$	р.	Outer orbital complex		
b.	$[\text{Co}(\text{C}_2\text{O}_4)_3]^{3-}$	q.	Inner orbital complex		
c.	[Fe(EDTA)] <sup>⊖</sup>	r.	$\mu = \sqrt{8}$ BM		
d.	$[Ni(en)_3]^{2+}$	s.	Shows optical activity		

22. Match the column.

	Column I		Column II
a.	MnO <sub>4</sub> <sup>⊖</sup>	p.	sp <sup>3</sup> -hybridisation
b.	CrO <sub>4</sub> <sup>2-</sup>	q.	Tetrahedral structure
c.	Cr <sub>2</sub> O <sub>7</sub> <sup>2-</sup>	r.	Diamagnetic but colourful species
d.	CrO <sub>2</sub> Cl <sub>2</sub>	S.	+6 oxidation state on central atom
		t.	all X–O bonds are identical (where X is central atom)

23. Match the column.

Column I			Column II				
a.	[Fe(CO) <sub>4</sub> ] <sup>2-</sup>	p.	Complex having lowest bond length of CO ligand				
b.	[V(CO) <sub>6</sub> ] <sup>⊙</sup>	q.	Follow Sidgwick's rule of EAN				
c.	$K[PtCl_3(C_2H_4)]$	r.	Synergic bonding is involved in complex/ion				
d.	[Fe(H <sub>2</sub> O) <sub>5</sub> NO]SO <sub>4</sub>	s.	Complex having highest bond length of CO ligand				
		t.	Organometallic compound				

24. Match the items given in column I with that in Column II and III.

Column I Compound		Column II  No. of unpaired €'s		Column III  Hybridisation shape & characteristics		
· [COF <sub>6</sub> ] <sup>3</sup> -	ii.	3	q.	$dsp^2$ , square planar		
$[Cu(NH_3)_4]^{2-}$	iii.	4	r.	$sp^3$ , tetrahedral		
• [Ni(CO) <sub>4</sub> ]	iv.	1	s.	Complex ion is formed in the brown ring test for $NO_3^{\Theta}$ ion		



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ith that in Column II and III. 25.

Match the i	items given in column I with that in Column II and III.		Column II		Column III
	Column I		No. of isomers		Type of isomerism
1000 mm	Compound	i.	1	p.	Optical
a. [Pt(NI	$H_3$ ) (N $H_2$ OH) (NO <sub>2</sub> ) (py)] $^{\oplus}$	ii.	3	q.	Trans
50 01	$(NH_3) (NH_2OH) (NO_2) (py)]^{\oplus}$ $l_2(NH_3)_4]^{\oplus} + Cl^{\ominus}$ $l_3 (NH_3)_3] + NH_3$				
(Num	ber of isomers obtained for the complex producty	iii.	Zero	r.	Geometrical
c. [Cr(ec	[dta]	iv.	2	s.	None
d. HN	Pt				
e.	H <sub>2</sub> N		,		
[Pt(gl)	$[y)_2]$ where gly = glycinato $\vdots$ $\vdots$ $\vdots$				2
	O _				

Match the items given in column I with that in Column II and III.

	Column I		Column II		Column III
	Ions in complex species		Electronic configuration in crystal field theory		No. of unpaired $\bar{e}$ 's
a.	Fe <sup>+2</sup> (In weak octahedral field ligand)	i.	$t_{2g}^4, e_g^{-1}$	p.	4
b.	Fe <sup>+2</sup> (In strong octahedral field ligand)	ii.	$t_{2g}^4, e_g^2$	q.	3
c.	Mn <sup>3+</sup> (In weak octahedral field ligand)	iii.	$t_{2g}^{6}$ , $e_{g}^{0}$	r.	Zero
d.	Mn <sup>3+</sup> (In strong octahedral field ligand)	iv.	$t_{2g}^{3}, e_{g}^{1}$	s.	2
è.	Cr <sup>3+</sup> (In weak and strong octahedral field ligand)	v.	$t_{2g}^{3}, e_{g}^{0}$		

27. Match the items given in column I with that in Column II and III

	Column I		Column II		Column III
	Compound		Electronic configuration in crystal field theory		CFSE (Crystal field spliting energy
a.	$[Cr(H_2O)_6]^{2+}$ (When $\Delta < p$ )	i.	$(e^2, t_2^3)$	_	0.64
b.	$[FeCl_4]^{\Theta}$ (When $\Delta < p$ )	ii.	$(e^2, t_2^0)$	p.	$-0.6  \Delta_0$
c.	$[\text{FeO}_4]^{2-} (\text{When } \Delta < p)$		(e, t <sub>2</sub> )	q.	$-1.6 \Delta_0 + P$
		iii.	$(t_{2g}^4, e_g^0)$	r.	Zero
d.	$[\operatorname{Cr}(\operatorname{NH}_3)_6]^{2+}$ (When $\Delta > p$ )	iv.	$(t^3 e^1)$		
			$(t_{2g}^{3}, e_{g}^{1})$	S.	$-1.2 \Delta_{\rm t}$

### **Numerical Value Type**

### Naming and Terminology

- 1. Give the number of ligand(s) in which donor atom is only N. NH<sub>2</sub>CH<sub>2</sub>COO<sup>⊖</sup>, en, dien, Py, EDTA, ph
- 2. Give number of non-classical ligand which are negative ligands.

$$\overset{\Theta}{\text{CN}}, \, \text{S}_2\text{O}_3^{\,\, 2-}, \, \text{C}_3\text{H}_5^{\,\, \Theta}, \, \text{C}_5\text{H}_5^{\,\, \Theta}.$$

3. Give the number of ligands which are negative as well as flexidentate.

$$CO_3^{2-}$$
,  $CH_3COO^{\Theta}$ ,  $X^{\Theta}$ ,  $H^{\Theta}$ ,  $SO_4^{2-}$ 

4. Give the number of ligands which are monodentate as well

$$\stackrel{\Theta}{\text{CN}}$$
,  $C_2O_4^{2-}$ ,  $S_2^{2-}$ ,  $NO_2^{\Theta}$ ,  $\stackrel{\Theta}{\text{OCN}}$ ,  $SCN^{\Theta}$ 

- $\overset{\bigcirc}{\text{CN}}$ ,  $\text{C}_2\text{O}_4^{\ 2^-}$ ,  $\text{S}_2^{\ 2^-}$ ,  $\text{NO}_2^{\ \ominus}$ ,  $\overset{\bigcirc}{\text{OCN}}$ ,  $\text{SCN}^{\ \ominus}$  **5.** Give the number of strong field ligand(s) from the following:
- $NH_3$ , en,  $Cl^{\Theta}$ ,  $CH_3COO^{\Theta}$ , CN, CO,  $NO_2^{\Theta}$ 6. Give the number of weak field ligand(s) from the following:
- $S^{2-}, \overset{\Theta}{OH}, Cl^{\Theta}, H_2O, Py, NO_2^{\Theta}, NO_3^{\Theta}$  7. The sum of primary and secondary valencies of chromium in the complex CrBr<sub>3</sub>.6NH<sub>3</sub> is:
- 8. Find the number of ligand(s) which is/are chelating. en, C<sub>2</sub>O<sub>4</sub><sup>2-</sup>, acac, DMG, gly, ph

Find the number of ligand(s) which is/are polydentate ligand.

How many coordinated water molecule(s) is/are present in hown ring complex?

 $\underset{\theta \text{ jon acts as ligand in the compound.} }{\text{he }_{\theta \text{ jon acts}}^{\text{godium nitroprusside}} \text{ is used to test } S^{2-} \text{ ion. How many CN}$ 

 $\mu_{\text{bidentate.}}^{\text{Give}}$  the number of ligand(s) which is/are ambidentate and

 $_{S}^{\circ}CN$ ,  $_{O}^{\circ}CN$ ,  $S_{2}O_{3}^{2-}$ ,  $C_{2}O_{4}^{2-}$ ,  $S^{2-}$ 

the number of ligand(s) which is/are non-classical  $\lim_{s \to 0} \frac{1}{s} = \frac{1}{s}$ 

 $^{\circ\circ}_{(0,N0,C_2H_4,C_3H_5^{\Theta},H^{\Theta})}$ 

Give the number of ligand(s) which are monodentate, neutral as well as non-classical ligand.

 $_{\text{CO, CN}}, S_2O_3^{2-}, PF_3$ 

Solve the number of ligands which are non-classical ligand and  $\pi$  donor as well as  $\pi$  acceptor ligand.

 $CO, PH_3, PF_3, C_3H_5^{\ominus}, C_5H_5^{\ominus}$ 

What are the values of m and n in the anionic species  $[V(CO)_m]^{n-}$ , if it is following Sidwick EAN rule and having octahedral shape?

17. Consider the following carbonyl complex compounds

(I)  $H_x$ Cr(CO)<sub>5</sub> (II)  $CO_2$ (CO)<sub>y</sub> (III) Mo(CO)<sub>z</sub>

then calculate the value of  $\left(\frac{x+y+z}{5}\right)$  is:

18. If x is total number of  $\pi$  bonds in ph (1,10-N, N-phenanthroline) and y is total number of lone pair e<sup>-</sup>'s in ph and  $\alpha$ -nitroso- $\beta$ -naphthol. Then calculate the value of  $\left(\frac{x+y}{4}\right)$ .

#### merism

19. Give the total number of possible isomers of  $[ZnBr_2F_2]^{2-}$ .

10. Give the number of pair of enantiomer of [Ma<sub>2</sub>b<sub>2</sub>cd].

11. Give the total number of isomer of [Be(gly)<sub>2</sub>].

22. How many pairs of enantiomers are possible for [M(AA) (BC)de]?

23. Find the number of geometrical isomers in  $[Co(en)(Pn) (NO_2)_2]$ .

 $e_{1} = \begin{array}{c|c} CH_{2} - CH_{2} & * \\ | & | & \\ H_{2}N & NH_{2} & Pn = \end{array} \begin{array}{c} * \\ NH_{2} - CH_{2} - CH_{-}NH_{2} \\ | & CH_{3} \end{array}$ 

4. Write the sum of geometrical isomers in

 $\begin{array}{l} [\text{Pt}(\text{H}_2\text{N-CH}(\text{CH}_3)\text{--COO})_2] \text{ complex and stereoisomers} \\ \text{of } [\text{Pt}(\text{gly})_3]^{\oplus} \text{ complex}. \end{array}$ 

25. Write the sum of geometrical isomer in [Ma<sub>2</sub>b<sub>2</sub>c<sub>2</sub>] complex and stereoisomers in [M(AB)<sub>3</sub>] complex.

- **26.** Give the ratio of geometrical isomers in  $[M(AA)_2b_2]$  and optical isomers of  $[M(AA)_3]$ .
- 27. Give the number of geometrical isomer in [Pt(gly)<sub>2</sub>].
- **28.** Give the total number of possible isomers of [Col<sub>2</sub>(CN)(NH<sub>2</sub>)en].
- **29.** Give the total number of possible isomers (*cis-trans* and optical) of  $[CrCl_2 en_2]^{\oplus}$ .
- **30.** Give the total number of possible structural isomers of the compound [Cu(NH<sub>3</sub>)<sub>4</sub>] [Pt I<sub>4</sub>].
- 31. Give the number of total possible coordination isomers in [Pt(NH<sub>3</sub>)<sub>4</sub>] [Cu(Br)<sub>4</sub>].
- 32. Give the number of total possible ionisation isomers in [Pt(NH<sub>3</sub>)<sub>4</sub>Cl<sub>2</sub>]Br<sub>2</sub>.
- 33. Give the ratio of trans-isomers in  $[M(AA)b_2c_2](A)$  and  $[Ma_4b_2](B)$ , respectively.

### Hybridisation, VBT, CFT and Applications

- **34.** In hexacyanidomanganate(II) ion the Mn atom assumes  $d^2sp^3$ -hybrid states. Then the number of unpaired electrons in the complex is:
- **35.** Give the number of unpaired electron(s) in the complex ion  $[CoCl_6]^{3-}$ .
- **36.** Predict the number of unpaired electrons in a tetrahedral  $d^6$  ion and in a square planar  $d^7$  ion.
- 37. Give the number of unpaired electron present in the d-orbitals (whose lobes are present along the axis) for the complex  $[Co(SCN)_4]^{2-}$ .
- **38.** Give the number of 3d electrons occupied in  $t_{2g}$  orbitals of hydrated  $Cr^{3+}$  ion (octahedral).
- **39.** How many unpaired electrons are present in  $e_g$  orbital of  $MnO_4^{\Theta}$ ?
- **40.** How many electrons are present in  $d_{z^2}$  orbital of [Ni(gly)<sub>2</sub>]?
- **41.** Give the total number of  $t_{2g}$  and  $e_g$  electrons in  $[NiF_6]^{2-}$ .
- **42.** How many electrons are present in *d*-orbitals which are present along the axis in  $[Ti(H_2O)_6]^{3+}$ ?
- **43.** If Hund's rule is violated, then how many unpaired electrons are present in  $[Cr(NH_3)_6]^{3+}$  complex ion?
- **44.** Give the number of unpaired electrons in  $t_{2g}$  set of d-orbitals in  $[Co(H_2O)_3F_3]$  complex.
- **45.** How many maximum atom(s) is/are present in same plane of Cr(CO)<sub>6?</sub>
- **46.** Find out the number of hydrogen bonds present in the structure of the nickel dimethylglyoxime complex.
- **47.** How many e 's are present in  $t_{2g}$  set of d-orbitals of central metal cation in  $[Fe(H_2O)_5NO]SO_4$  brown ring complex.

### **Archives**

### JEE MAIN

### Single Correct Answer Type

- 1. Which of the following has an optical isomer?
  - (1)  $[Co(NH_3)_3Cl]^+$
- (2)  $[Co(en)(NH_3)_2]^{2+}$
- (3)  $[Co(H_2O)_4(en)]^{3+}$
- $(4) \left[ \text{Co(en)}_2 (\text{NH}_3)_2 \right]^{3+}$

(AIEEE 2009)

- 2. Which of the following pairs represents linkage isomers?
  - (1)  $[Cu(NH_3)_4]$   $[PtCl_4]$  and  $[Pt(NH_3)_4]$   $[CuCl_4]$
  - (2)  $[Pd(PPh_3)_2 (NCS)_2$  and  $[Pd(PPh_3)_2 (SCN)_2]$
  - (3)  $[Co(NH_3)_5] NO_3SO_4$  and  $[Co(NH_3)_5SO_4]NO_3$
  - (4)  $[PtCl_2(NH_3)_4]Br$  and  $[PtBr_2(NH_3)_4Cl_2$

(AIEEE 2009)

- 3. Which of the following has an optical isomer? (en = ethylenediamine)
  - (1)  $[Zn(en)(NH_3)_5]^{2+}$
- $(2)\left[\operatorname{Co}(\operatorname{en})_{3}\right]^{3+}$
- (3)  $[Co(H_2O)_4(en)]^{3+}$
- $(4) [Zn(en)_2]^{2+}$

(AIEEE 2010)

- 4. Which one of the following complex ions has geometrical isomers?
  - (1)  $[Co(en)_3]^{3+}$
- $(2) [Ni(NH_3)_5Br]^+$
- (3)  $[Co(NH_3)_2(en)_2]^{3+}$
- $(4) \left[ Cr(NH_3)_4(en) \right]^{3+}$

(AIEEE 2011)

- 5. Which of the following facts about the complex [Cr(NH<sub>3</sub>)<sub>6</sub>] Cl<sub>3</sub> is wrong?
  - (1) The complex involves  $d^2sp^3$  hybridization and is octahedral in shape.
  - (2) The complex is paramagnetic.
  - (3) The complex is an outer orbital complex.
  - (4) The complex gives white precipitate with silver nitrate (AIEEE 2011) solution.
- 6. The magnetic moment (spin only) of  $[NiCl_4]^{2+}$  is:
  - (1) 1.82 BM
- (2)5.46 BM
- (3) 2.82 BM
- (4) 1.41 BM (AIEEE 2011)
- 7. Among the ligands NH<sub>3</sub>, en, CN<sup>-</sup> and CO, the correct order of their increasing field strength is
  - (1)  $CO < NH_3 < en < CN^-$
- (2)  $NH_3 < en < CN^- < CO$
- (3)  $CN^- < NH_3 < CO < en$
- $(4) en < CN^- < NH_3 < CO$
- (AIEEE 2011)

8. Which among the following will be named as dibromidobis-(ethylenediamine) chromium (III) bromide?

- (1)  $[Cr(en)_3]Br_3$
- (2) [Cr(en)<sub>2</sub>Br<sub>2</sub>]Br
- (3)  $[Cr(en)Br_4]^-$
- (4) [Cr(en)Br<sub>2</sub>]Br
- (AIEEE 2012)

9. Which of the following complex species is not expected to exhibit optical isomerism?

- (1)  $[Co(en)_3Cl_2]^+$
- $(2) [Co(en)_{2}Cl_{2}]^{+}$
- (3)  $[Co(NH_3)_3Cl_3]$
- (4)  $[Co(en)(NH_3)Cl_2]^+$

(JEE Main 2013)

- 10. The equation which is balanced and represents the correct product(s) is
  - (1)  $\text{Li}_2\text{O} + 2\text{KCl} \longrightarrow 2\text{LiCl} + \text{K}_2\text{O}$
  - (2)  $[CoCl(NH_3)_5]^+ + 5H^+ \longrightarrow CO^{2+} + 5NH_4^+ + Cl^-$
  - (3)  $[Mg(H_2O)_6]^{2+} + (EDTA)^{4-} \xrightarrow{\text{excess NaOH}}$

 $[Mg(EDTA)]^{2+} + 6H_{2}O$ 

(4)  $CuSO_4 + 4KCN \longrightarrow K_2[Cu(CN)_4] + K_2SO_4$ 

(JEE Main 2014)

- 11. The octahedral complex of a metal ion  $M^{3+}$  with four monodentate ligands  $L_1$ ,  $L_2$ ,  $L_3$  and  $L_4$  absorbs wavelengths in the region of red, green, yellow, and blue, respectively The increasing order of ligand strength of the four ligands is:
  - $(1) L_4 < L_3 < L_2 < L_1$
- $(2)L_1 < L_3 < L_2 < L_4$
- $(3) L_3 < L_2 < L_4 < L_1$
- $(4) L_1 < L_2 < L_4 < L_2$

(JEE Main 2014)

- 12. The number of geometric isomers that can exist for square planar  $[Pt(Cl)(py)(NH_3)(NH_2OH)]^+$  is (py = pyridine):
  - (1)2

(2)3

(3)4

(4)6

(JEE Main 2015)

- 13. Which of the following compounds is not colored yellow?
  - $(1) \operatorname{Zn}_{2}[\operatorname{Fe}(\operatorname{CN})_{6}]$
- $(2) K_3 [Co(NO_2)_6]$
- (3) (NH<sub>4</sub>)<sub>3</sub> [As(Mo<sub>3</sub>O<sub>10</sub>)<sub>4</sub>
- (4) BaCrO<sub>4</sub>

- (JEE Main 2015)
- 14. Which one of the following complexes shows optical isomerism?
  - (1)  $[Co(NH_3)_4Cl_5]Cl$
- $(2) [Co(NH_3)_3Cl_3]$
- (3) *cis* [Co(*en*),Cl,]Cl
- (4) trans [Co(en)2Cl2]Cl

(en = ethylenediamine)

(JEE Main 2016)

15. The pair having the same magnetic moment is:

[At. No.: Cr = 24, Mn = 25, Fe = 26, Co = 27]

- (1)  $[CoCl_4]^{2-}$  and  $[Fe(H,O)_6]^{2+}$
- (2)  $[Cr(H_2O)_6]^{2+}$  and  $[CoCl_4]^{2-}$
- (3)  $[Cr(H_2O)_6]^{2+}$  and  $[Fe(H_2O)_6]^{2+}$
- (4)  $[Mn(H_2O)_6]^{2+}$  and  $[Cr(H_2O)_6]^{2+}$

(JEE Main 2016)

- 16. On treatment of 100 mL of 0.1 M solution of CoCl<sub>3</sub>.6H<sub>2</sub>O with excess AgNO<sub>3</sub>,  $1.2 \times 10^{22}$  ions are precipitated. The complex is:
  - (1)  $[Co(H_2O)_4Cl_2]Cl.2H_2O$
- $(2)[Co(H_2O)_3Cl_3].3H_2O$
- (3) [Co(H<sub>2</sub>O)<sub>6</sub>]Cl<sub>3</sub>
- $(4)[Co(H_2O)_5Cl]Cl_2.H_2O$

(JEE Main 2017)

The oxidation states of Cr in  $[Cr(H_2O)_6]Cl_3$ ,  $[Cr(C_6H_6)_2]$ , and  $K_2[Cr(CN)_2(O)_2(O_2)(NH_2)]$  respectively and  $K_2[Cr(CN)_2(O)_2(O_2)(NH_3)]$  respectively are:

 $(1)^{+3}$ , +2, and +4

(2)+3, 0, and +6

(3)+3, 0, and +4

(4)+3, +4, and +6

(**JEE Main 2018**)

Consider the following reaction and statements:

 $[Co(NH_3)_4Br_2]^+ + Br^- \rightarrow [Co(NH_3)_3Br_3] + NH_3$ 

- (1) Two isomers are produced if the reactant complex ion is a cis-isomer.
- (II) Two isomers are produced if the reactant complex ion is a trans-isomer.
- (III) Only one isomer is produced if the reactant complex ion is a trans-isomer.
- (IV) Only one isomer is produced if the reactant complex ion is a cis-isomer.

The correct statements are:

(1) (I) and (III)

(2) (III) and (IV)

(3) (II) and (IV)

(4)(I) and (II)

(JEE Main 2018)

#### **IEE ADVANCED**

#### single Correct Answer Type

1. The correct structure of ethylenediamineteraacetic acid (EDTA) is

$$\begin{array}{c} \text{HOOC-H}_2\text{C} \\ \text{HOOC-H}_2\text{C} \end{array} \text{N-CH=CH-N} \begin{array}{c} \text{CH}_2\text{-COOH} \\ \text{CH}_2\text{-COOH} \end{array}$$

(IIT-JEE 2010)

2. The ionisation isomer of  $[Cr(H_2O)_4Cl(NO_2)]Cl$  is

(1) [Cr(H<sub>2</sub>O)<sub>4</sub>(O<sub>2</sub>N)]Cl<sub>2</sub>

 $(2) \left[ Cr(H<sub>2</sub>O)_{4}Cl_{2} \right] (NO_{2})$ 

(3) [Cr(H<sub>2</sub>O)<sub>4</sub>Cl(ONO)]Cl

(4) [Cr(H<sub>2</sub>O)<sub>4</sub>Cl<sub>2</sub>(NO<sub>2</sub>)]H<sub>2</sub>O

(IIT-JEE 2010)

- 3. The complex showing a spin-magnetic moment of 2.82 BM
  - (1) Ni(CO)<sub>4</sub>
- $(2)[NiCl_4]^{2-}$
- $(3) \text{Ni}(PPh_3)_4$
- $(4) [Ni(CN)_{4}]^{2}$

(IIT-JEE 2010)

- 4. Geometrical shapes of the complexes formed by the reaction of Ni<sup>2+</sup> with Cl<sup> $\Theta$ </sup>, CN<sup> $\Theta$ </sup> and H<sub>2</sub>O, respectively, are
  - (1) Octahedral, tetrahedral and square planar
  - (2) Tetrahedral, square planar and octahedral
  - (3) Square planar, tetrahedral and octahedral
  - (4) Octahedral, square planar and octahedral

(IIT-JEE 2011)

5. Among the following complexes (K-P)

 $K_3[Fe(CN)_6]$  (**K**),  $[Co(NH_3)_6]Cl_3$  (**L**),

 $Na_3[Co(oxalate)_3]$  (M),  $[Ni(H_2O)_6]Cl_2(N)$ ,

 $[Pt(CN)_4]$  (O) and  $[Zn(H_2O)_6]$  (NO<sub>3</sub>)<sub>2</sub>(P)

The diamagnetic complexes are

(1) K, L, M, N

(2) K, M, O, P

(3) L, M, O, P

(4) L, M, N, O

(IIT-JEE 2011)

- 6. As per IUPAC nomenclature, the name of the complex  $[Co(H_2O)_4(NH_3)_2]Cl_3$  is
  - (1) Tetaaquadiaminecobalt(III) chloride
  - (2) Tetraaquadiamminecobalt(III) chloride
  - (3) Diaminetetraaquacobalt(III) chloride
  - (4) Diamminetetraaquacobalt(III) chloride

(IIT-JEE 2012)

- 7. The colour of light absorbed by an aqueous solution of CuSO<sub>4</sub> is
  - (1) orange-red
- (2) blue-green

(3) yellow

(4) violet

(IIT-JEE 2012)

- 8.  $[NiCl_2{P(C_2H_5)_2(C_6H_5)}_2]$  exhibits temperature dependent magnetic behaviour (paramagnetic/diamagnetic). The coordination geometries of Ni2+ in the paramagnetic and diamagnetic states are respectively
  - (1) Tetrahedral and tetrahedral
  - (2) Square planar and square planar
  - (3) Tetrahedral and square planar
  - (4) Square planar and tetrahedral

(IIT-JEE 2012)

- 9. Which of the following complexes is **not** expected to exhibit optical isomerism?
  - (1) [Co(en)<sub>2</sub>Cl<sub>2</sub>]<sup>⊕</sup>
- (2)  $[Co(NH_3)_3Cl_3]$
- (3)  $[Co(en) (NH_3)_2 Cl_2]^{\oplus}$
- (4)  $[Co(en)_3]^{3+}$

(JEE Advanced 2013)

10. Consider the following complexes ions, P, Q and R

 $\mathbf{P} = [\text{FeF}_6]^{3-}, \mathbf{Q} = [\text{V(H}_2\text{O)}_6]^{2+} \text{ and } \mathbf{R} = [\text{Fe(H}_2\text{O)}_6]^{2+}$ 

The correct order of the complex ions, according to their spin only magnetic moment values (in BM) is

- (1) R < Q < P
- (2) Q < R < P
- (3) R < P < O
- (4) Q < P < R

(JEE Advanced 2013)

11. An excess of  $AgNO_3$  is added to  $100 \, mL$  of a 0.01 M solution of dichlorotetraaquachromium(III) chloride. The number of moles of AgCl precipitated would be

(1) 0.003

(2) 0.01

(3) 0.001

(4) 0.002

### (JEE Advanced 2013)

12. The equation which is balanced and represents the correct product(s) is

(1)  $[Mg(H_2O)_6]^{2^+} + (EDTA)^{4^-} \xrightarrow{Excess NaOH} [Mg(EDTA)]^{2^+} + 6H_2O$ 

(2)  $CuSO_4 + 4 KCN \longrightarrow K_2[Cu(CN)_4] + K_2SO_4$ 

(3) Li<sub>2</sub>O + 2 KCl  $\longrightarrow$  2LiCl + K<sub>2</sub>O

 $(4) \left[ \text{CoCl(NH}_3)_5 \right]^{\oplus} + 5\text{H}^{\oplus} \longrightarrow \text{Co}^{2+} + 5\text{NH}_4^{\oplus} + \text{Cl}^{\Theta}$ 

### (JEE Advanced 2014)

- 13. The number of geometric isomers that can exist for square planar  $[Pt(Cl)(py)(NH_3)(NH_2OH)]^{\oplus}$  is (py = pyridine):

(2) 3

(3)4

(4)6

### (JEE Advanced 2015)

14. Among [Ni(CO)<sub>4</sub>], [NiCl<sub>4</sub>]<sup>2-</sup>, [Co(NH<sub>3</sub>)<sub>4</sub>Cl<sub>2</sub>]Cl, Na<sub>3</sub>[CoF<sub>6</sub>], Na<sub>2</sub>O<sub>2</sub> and CsO<sub>2</sub>, the total number of paramagnetic compounds is

(1)2

(2)3

(3)4

(4)5 (JEE Advanced 2016)

- 15. The geometries of the ammonia complexes of  $Ni^{2+}$ ,  $Pt^{2+}$  and Zn<sup>2+</sup>, respectively, are
  - (1) octahedral, square planar and tetrahedral
  - (2) square planar, octahedral and tetrahedral
  - (3) tetrahedral, square planar and octahedral
  - (4) octahedral, tetrahedral and square planar

(JEE Advanced 2016)

### **Multiple Correct Answers Type**

- 1. The pair of coordination complexes/ions exhibiting the same kind of isomerism is (are)
  - (1)  $[Cr(NH_3)_5Cl]Cl_2$  and  $[Cr(NH_3)_4Cl_2]Cl$
  - (2)  $[Co(NH_3)_4Cl_2]^{\oplus}$  and  $[Pt(NH_3)_2(H_2O)Cl]^{\oplus}$
  - (3)  $[CoBr_2Cl_2]^{2-}$  and  $[PtBr_2Cl_2]^{2-}$
  - (4)  $[Pt(NH_3)_3(NO_3)]Cl$  and  $[Pt(NH_3)_3Cl]Br$

### (JEE Advanced 2013)

2. Addition of excess aqueous ammonia to a pink coloured aqueous solution of MCl<sub>2</sub>.6H<sub>2</sub>O(X) and NH<sub>4</sub>Cl gives an octahedral complex Y in the presence of air. In aqueous solution, complex Y behaves as 1:3 electrolyte. The reaction of X with excess HCl at room temperature results in the formation of a blue coloured complex Z. The calculated spin only magnetic moment of X and Z is 3.87 B.M., whereas it is zero for complex Y.

Among the following options, which statement(s) is(are) correct?

- (1) The hybridization of the central metal ion in Y is  $d^2sp^3$ .
- (2) Z is a tetrahedral complex
- (3) Addition of silver nitrate to Y gives only two equivalents of silver chloride.

- (4) When **X** and **Z** are in equilibrium at 0°C, the colour of the (JEE Advanced 2017) solution is pink
- 3. The correct option(s) regarding the complex [Co (en) (NH<sub>3</sub>)<sub>3</sub>  $(H_2O)]^{3+}$  (en =  $H_2NCH_2CH_2NH_2$ ) is (are)
  - (1) It has two geometrical isomers
  - (2) It will have three geometrical isomers if bidentate 'en' is replaced by two cyanide ligands
  - (3) It is paramagnetic
  - (4) It absorbs light at longer wavelength as compared to (JEE Advanced 2018)  $[Co(en)(NH_2)_4]^{3+}$

### **Linked Comprehension Type**

### Paragraph 1

The coordination number of Ni<sup>2+</sup> is 4.

 $NiCl_2 + KCN(excess) \rightarrow A (cyano complex)$ 

 $NiCl_2 + conc. HCl (excess) \rightarrow B (Chloro complex)$ 

- 1. The IUPAC name of A and B are
  - (1) potassium tetracyanonickelate (II), potassium tetrachloronickelate (II).
  - (2) tetracyanopotassiumnickelate (II). tetrrachloropotassiumnickelate (II).
  - (3) tetracyanonickel(II) tetrachloronickel(II)
  - (4) potassium tetracyanonickel(II), tetracholoronickel(II),
- 2. Predict the magnetic nature of A and B:
  - (1) Both are diamagnetic.
  - (2) A is diamagnetic and B is paramagnetic with one unpaired
  - (3) A is diamagnetic and B is paramagnetic with two unpaired electrons.
  - (4) Both are paramagnetic.
- 3. The hybridisation of A and B are

(1)  $dsp^2$ ,  $sp^3$ 

 $(3) dsp^2, dsp^2$ 

(2)  $sp^3$ ,  $sp^3$ (4)  $sp^3d^2$ ,  $d^2sp^3$ 

(IIT-JEE 2006)

### Paragraph 2

An aqueous solution of metal ion M1 reacts separately with reagents  ${\bf Q}$  and  ${\bf R}$  in excess to give tetrahedral and square planar complexes, respectively. An aqueous solution of another metal ion M2 always forms tetrahedral complexes with these reagents. Aqueous solution of M2 on reaction with reagent S gives white precipitate which dissolves in excess of S. The reactions are summarised in the scheme given below:

### **SCHEME:**

Tetrahedral  $\leftarrow \frac{Q}{excess}$  M1  $\rightarrow \frac{R}{excess}$  Square Planar

Tetrahedral  $\leftarrow$   $\stackrel{Q}{\leftarrow}$   $\stackrel{M2}{\leftarrow}$   $\stackrel{R}{\leftarrow}$  Tetrahedral  $\stackrel{S}{\leftarrow}$  stoichiometric amount  $\stackrel{S}{\leftarrow}$  precipitate dissolves

M1, Q and R, respectively are

 $(1) Zn^{2+}$ , KCN and HCl

(2) Ni<sup>2+</sup>, HCl and KCN

 $^{(3)}$ Cd<sup>2+</sup>, KCN and HCl

(4) Co<sup>2+</sup>, HCl and KCN

Reagent S is

 $(1) K_4[Fe(CN)_6]$ 

(2) Na<sub>2</sub>HPO<sub>4</sub>

(3)  $K_2$ CrO<sub>4</sub>

(4) KOH

<sub>Matrix</sub> Match Type

(JEE Advanced 2014)

1. Match the complexes in Column I with their properties listed in Column II.

	Column I		Column II
a.	[Co(NH <sub>3</sub> ) <sub>4</sub> (H <sub>2</sub> O) <sub>2</sub> ]Cl <sub>2</sub>	p.	Geometrical isomers
b.	[Pt(NH <sub>3</sub> ) <sub>2</sub> Cl <sub>2</sub> ]	q.	Paramagnetic
c.	[Co(H <sub>2</sub> O) <sub>5</sub> Cl]Cl	r.	Diamagnetic
d.	[Ni(H <sub>2</sub> O) <sub>6</sub> ]Cl <sub>2</sub>	s.	Metal ion with +2 oxidation state

#### (IIT-JEE 2007)

 Match each coordination compound in Column I with an appropriate pair of characteristics from Column II and select the correct answer using the code given below the lists.

	Column I		Column II
2.	[Cr(NH <sub>3</sub> ) <sub>4</sub> Cl <sub>2</sub> ]Cl	p.	Paramagnetic and exhibits ionisation isomerism
b.	[Ti(H <sub>2</sub> O) <sub>5</sub> Cl](NO <sub>3</sub> ) <sub>2</sub>	q.	Diamagnetic and exhibits cis-trans isomerism
c.	[Pt(en) (NH <sub>3</sub> )Cl]NO <sub>3</sub>	r.	Paramagnetic and exhibits cis-trans isomerism
d.	[Co(NH <sub>3</sub> ) <sub>4</sub> (NO <sub>3</sub> ) <sub>2</sub> ]NO <sub>3</sub>	s.	Diamagnetic and exhibits ionisation isomerism

### Code:

	a	b	c	d
(1)	S	q	r	p

(2) r p s q

(3) q p r s (4) p r s q

(JEE Advanced 2014)

3. Match the catalysts to the correct processes:

	Catalyst		Process
a.	TiCl <sub>3</sub>	i.	Wacker process
b.	PdCl <sub>2</sub>	ii.	Ziegler-Natta polymerization
c.	CuCl <sub>2</sub>	iii.	Contact process
d.	V <sub>2</sub> O <sub>5</sub>	iv.	Deacon's process

(1) a. -iii., b. -ii., c. -iv., d. -i.

(2) a. - ii., b. - i., c. - iv., d. - iii.

(3) a. - ii., b. - iii., c. - iv., d. - i.

(4) a. -iii., b. -i., c. -ii., d. -iv.

(JEE Advanced 2015)

**4.** Match each set of hybrid orbitals from List-I with complex(es) given List-II.

List-I	List-II
P.  dsp2	1. [FeF <sub>6</sub> ] <sup>4-</sup>
$\mathbf{Q}.  sp^3$	<b>2.</b> [Ti(H <sub>2</sub> O) <sub>3</sub> Cl <sub>3</sub> ]
$\mathbf{R.}  sp^3d^2$	3. [Cr(NH <sub>3</sub> ) <sub>6</sub> ] <sup>3+</sup>
S. $d^2sp^3$	4. [FeCl <sub>4</sub> ] <sup>2-</sup>
	5. Ni(CO) <sub>4</sub>
	<b>6.</b> [Ni(CN) <sub>4</sub> ] <sup>2-</sup>

The correct option is

(1)  $P \rightarrow 5$ ;  $Q \rightarrow 4$ , 6;  $R \rightarrow 2$ , 3;  $S \rightarrow 1$ 

(2)  $P \to 5$ , 6;  $Q \to 4$ ;  $R \to 3$ ;  $S \to 1$ , 2

(3)  $P \rightarrow 6$ ;  $Q \rightarrow 4$ , 5;  $R \rightarrow 1$ ;  $S \rightarrow 2$ , 3

(3)  $P \rightarrow 4, 6; Q \rightarrow 5, 6; R \rightarrow 1, 2; S \rightarrow 3$ 

(JEE Advanced 2018)

### **Numerical Value Type**

1. The volume (in mL) of  $0.1 \text{M AgNO}_3$  required for complete precipitation of  $\text{Cl}^{\Theta}$  ions present in 30 mL of 0.01 M solution of  $[\text{Cr}(\text{H}_2\text{O})_5\text{Cl}]\text{Cl}_2$ , as silver chliride is close to

(IIT-JEE 2011)

2. EDTA<sup>4-</sup> is ethylenediamine tetraacetate ion. The total number of N-Co-O bond angles in [Co(EDTA)]<sup>-1</sup> complex ion is

(JEE Advanced 2013)

3. In the complex acetylbromidodicarbonylbis (triethylphosphine) iron(II), the number of Fe–C bond(s) is (JEE Advanced 2015)

**4.** Among the complex ions,  $[Co(NH_2-CH_2-CH_2-NH_2)_2Cl_2]^+$ ,  $[CrCl_2(C_2O_4)_2]^{3-}$ ,  $[Fe(H_2O)_4(OH)_2]^+$ ,  $[Fe(NH_3)_2(CN)_4]^-$ ,  $[Co(NH_2-CH_2-CH_2-NH_2)_2(NH_3)Cl]^{2+}$  and  $[Co(NH_3)_4(H_2O)Cl]^{2+}$ , the number of complex ion(s) that show(s) cis-trans isomerism is

(JEE Advanced 2015)

5. In dilute aqueous  $H_2SO_4$ , the complex diaquodioxalatoferrate(II) is oxidized by  $MnO_4^{\odot}$ . For this reaction, the ratio of the rate of change of  $[H^{\oplus}]$  to the rate of change of  $[MnO_4^{\odot}]$  is (JEE Advanced 2015)

6. For the octahedral complexes of Fe<sup>3+</sup> in SCN<sup>©</sup> (thiocyanato–S) and in CN<sup>-</sup> ligand environments, the

**116.** (2)

**121.**(1)

**126.** (3)

**131.** (1)

**136.** (4)

**141.** (4)

**146.** (2)

**151.** (2)

**156.** (2)

**161.** (1)

**166.** (2)

**171.** (1)

**176.**(1)

**181.** (3)

**117.** (1)

**122.** (1)

**127.** (2)

**132.** (1)

**137.** (3)

**142.** (3)

**147.** (3)

**152.** (1)

**157.** (2)

**162.** (4)

**167.** (1)

**172.** (3)

**177.** (2)

**182.** (3)

difference between the spin-only magnetic moments in Bohr magnetons (when approximated to the nearest integer) is [Atomic number of Fe = 26]

(JEE Advanced 2015)

7. If the freezing point of a 0.01 molal aqueous solution of a cobalt (III) chloride-ammonia complex (which behaves as a strong electrolyte) is -0.0558°C, the number of chloride(s) in the coordination sphere of the complex is

 $[K_f \text{ of water} = 1.86 \text{ K kg mol}^{-1}]$ 

(JEE Advanced 2015) 8. The number of geometric isomers possible for the complex  $[CoL_2Cl_2]$  (L =  $H_2NCH_2CH_2O$ ) is

(JEE Advanced 2016)

## **Answers Key**

EXERCISES				
Single Cor	rect Answer		4 (4)	<b>5.</b> (3)
1.(2)	<b>2.</b> (4)	<b>3.</b> (1)	<b>4.</b> (4)	<b>10.</b> (2)
6. (2)	<b>7.</b> (1)	<b>8.</b> (4)	<b>9.</b> (1)	15. (4)
11. (2)	<b>12.</b> (1)	<b>13.</b> (3)	<b>14.</b> (3)	<b>20.</b> (1)
<b>16.</b> (1)	<b>17.</b> (2)	<b>18.</b> (1)	<b>19.</b> (3)	
<b>21.</b> (1)	<b>22.</b> (2)	<b>23.</b> (1)	<b>24.</b> (3)	<b>25.</b> (2)
<b>26.</b> (3)	<b>27.</b> (2)	<b>28.</b> (1)	<b>29.</b> (3)	<b>30.</b> (3)
<b>31.</b> (3)	<b>32.</b> (3)	<b>33.</b> (4)	<b>34.</b> (3)	<b>35.</b> (4)
<b>36.</b> (2)	<b>37.</b> (1)	<b>38.</b> (1)	<b>39.</b> (1)	<b>40.</b> (4)
<b>41.</b> (2)	<b>42.</b> (2)	<b>43.</b> (4)	<b>44.</b> (2)	<b>45.</b> (4)
<b>46.</b> (2)	<b>47.</b> (2)	<b>48.</b> (3)	<b>49.</b> (1)	<b>50.</b> (3)
<b>51.</b> (1)	<b>52.</b> (2)	<b>53.</b> (3)	<b>54.</b> (3)	<b>55.</b> (3)
<b>56.</b> (3)	<b>57.</b> (3)	<b>58.</b> (2)	<b>59.</b> (1)	<b>60.</b> (2)
<b>61.</b> (3)	<b>62.</b> (2)	<b>63.</b> (1)	<b>64.</b> (2)	<b>65.</b> (3)
<b>66.</b> (2)	<b>67.</b> (2)	<b>68.</b> (2)	<b>69.</b> (2)	<b>70.</b> (1)
<b>71.</b> (3)	<b>72.</b> (3)	<b>73.</b> (3)	<b>74.</b> (2)	75. (4)
<b>76.</b> (2)	77. (2)	<b>78.</b> (2)	<b>79.</b> (3)	<b>80.</b> (3)
<b>81.</b> (4)	<b>82.</b> (4)	<b>83.</b> (4)	<b>84.</b> (4)	<b>85.</b> (1)
<b>86.</b> (1)	<b>87.</b> (2)	<b>88.</b> (4)	<b>89.</b> (1)	<b>90.</b> (4)
<b>91.</b> (3)	<b>92.</b> (2)	<b>93.</b> (2)	<b>94.</b> (2)	<b>95.</b> (3)
<b>96.</b> (4)	<b>97.</b> (3)	<b>98.</b> (4)	<b>99.</b> (2)	<b>100.</b> (4)
<b>101.</b> (2)	<b>102.</b> (1)	<b>103.</b> (3)	<b>104.</b> (1)	<b>105.</b> (2)
<b>106.</b> (1)	<b>107.</b> (2)	<b>108.</b> (3)	<b>109.</b> (2)	110. (4)
<b>111.</b> (4)	<b>112.</b> (2)	<b>113.</b> (3)	<b>114.</b> (2)	115. (4)
				` '

**118.** (3)

**123.** (3)

**128.** (1)

**133.** (3)

**138.** (1)

**143.** (3)

**148.** (1)

**153.** (2)

**158.** (2)

**163.** (1)

**168.** (2)

**173.** (1)

**178.** (3)

**183.** (1)

**119.** (1)

**124.** (2)

**129.** (4)

**134.** (1)

**139.** (3)

**144.** (1)

149. (4)

**154.** (3)

**159.** (3)

**164.** (1)

**169.** (1)

174. (4)

**179.** (1)

**120.** (1)

**125.** (1)

**130.** (2)

135.(1)

**140.**(1)

**145.** (2)

**150.** (2)

**155.** (3)

**160.** (1)

165. (4)

**170.** (3)

175.(1)

**180.** (1)

Multiple Correct A	nswers Type	
	<b>2.</b> (1, 2, 3)	<b>3.</b> (1, 2)
1. (1, 2) 4. (1, 2, 3, 4)	<b>5.</b> (1, 2, 3)	<b>6.</b> (1, 2, 3)
7. (1, 2, 3, 4)	<b>8.</b> (1, 2, 3)	<b>9.</b> (1, 2, 3)
<b>10.</b> (1, 2, 3, 4)	<b>11.</b> (1,2,3)	<b>12.</b> (1, 3, 4)
<b>13.</b> (1, 2, 3)	<b>14.</b> (2, 3, 4)	<b>15.</b> (1, 4)
<b>16.</b> (2,3,4)	<b>17.</b> (2, 3, 4)	<b>18.</b> (1, 2, 3) <b>21.</b> (2, 3)
<b>19.</b> (1, 2, 3)	<b>20.</b> (2, 3) <b>23.</b> (2, 3)	<b>24.</b> (1, 2, 3, 4)
<b>22.</b> (1) <b>25.</b> (1, 4)	<b>26.</b> (1, 2, 4)	<b>27.</b> (1, 2, 3, 4)
<b>28.</b> (2, 3, 4)	<b>29.</b> (1, 2, 4)	<b>30.</b> (2, 4)
<b>31.</b> (2, 3, 4)	<b>32.</b> (2, 3)	<b>33.</b> (1, 2, 4)
<b>34.</b> (3, 4)	<b>35.</b> (1, 2, 3)	<b>36.</b> (2, 3, 4)
<b>37.</b> (1, 3, 4)	<b>38.</b> (1, 2)	<b>39.</b> (1, 2)
<b>40.</b> (2, 3, 4)	<b>41.</b> (2, 3)	<b>42.</b> (1, 2, 3, 4) <b>45.</b> (1, 2, 4)
<b>43.</b> (1, 2, 3, 4)	<b>44.</b> (1, 2, 3) <b>47.</b> (1, 2, 3)	<b>48.</b> (1, 2, 4)
<b>46.</b> (1, 2) <b>49.</b> (1, 2)	<b>50.</b> (1, 2, 3)	<b>51.</b> (2, 3, 4)
<b>52.</b> (2, 3, 4)	<b>53.</b> (1, 2, 3)	<b>54.</b> (1, 2)

### **Linked Comprehension Type**

		, .		
<b>1.</b> (1)	<b>2.</b> (2)	<b>3.</b> (2)	<b>4.</b> (3)	<b>5.</b> (2)
<b>6.</b> (2)	7. (3)	<b>8.</b> (1)	<b>9.</b> (2)	<b>10.</b> (1)
<b>11.</b> (3)	<b>12.</b> (1, 4)	<b>13.</b> (2, 3,	4) <b>14.</b> (3, 4)	<b>15.</b> (2)
<b>16.</b> (2)	<b>17.</b> (2)	<b>18.</b> (4)	<b>19.</b> (1)	<b>20.</b> (3)
<b>21.</b> (4)	<b>22.</b> (2)	<b>23.</b> (4)	<b>24.</b> (3)	<b>25.</b> (1)
<b>26.</b> (3)	<b>27.</b> (1)	<b>28.</b> (3)	<b>29.</b> (1)	<b>30.</b> (1)
<b>31.</b> (1)	<b>32.</b> (1)	<b>33.</b> (3)	<b>34.</b> (4)	35. (4)
<b>36.</b> (4)	<b>37.</b> (4)	<b>38.</b> (1)	<b>39.</b> (2)	<b>40.</b> (1)
<b>41.</b> (4)	<b>42.</b> (3)	<b>43.</b> (3)		

### Matrix Match Type

Q.No.	a	b	c	d	e t
1.	q	p, q, r	q	p, q, s	
2.	S	р	q	r	
3.	q, r, s	p, q, r, s	p, r	p, r, t	
4.	p, q, r	s,	р	q; s	
5.	p, s	p, s, t	s, t	p, s	
6.	s	р	q	_	

de(s)	. /	r,s	р	р				26 (4.1)			Coordination (	Compounds 7.127
(8		1. r	р	t	_	_	_	<b>36.</b> (4,1) <b>41.</b> (6)	<b>37.</b> (0)	<b>38.</b> (3)	<b>39.</b> (0)	<b>40.</b> (2)
		g. p, r, s			q	_	_	<b>46.</b> (2)	<b>42.</b> (0) <b>47.</b> (5)	<b>43.</b> (1)	<b>44.</b> (2)	<b>45.</b> (9)
)15)	9	), p, s, p	r	p, q	q	_	_	(2)	47.(3)			
$g_{e_{k}}$	[ 1]	0. <b>p</b>	p, q, s, t	t	p	_	_					
·X	11			p, r, s	1, 4, 5,	_	_	ARCHIVES				
(6)	12	p, s, t	p, r, t	p, q, t	р	_	_	JEE Main				
	13.		q, r	p, r, s	q, r	_	_	Single Corre	ct Answei	r Type		
	14.	r, s	q	S	p	_	_	1. (4)	<b>2.</b> (2)	<b>3.</b> (2)	4 (2)	<b>5</b> (2)
	15.	r, s	p, q	t	S	_	_	<b>6.</b> (3)	7. (2)	<b>8.</b> (2)	<b>4.</b> (3) <b>9.</b> (3)	<b>5.</b> (3) <b>10.</b> (2)
	16.	p, q, t	p, q, r, s, t	r, s, t	p, r, s, t	_		11. (2)	<b>12.</b> (2)	<b>13.</b> (1)	<b>14.</b> (3)	<b>15.</b> (3)
	17.	q, r	p, q, r	r, s	r, s	-	_	<b>16.</b> (4)	<b>17.</b> (2)	<b>18.</b> (1)	1 (3)	13. (3)
	18.	p, t	p, r, t	p, r, t	q, s	-	-	JEE Advance	d			
	19.	p, q, r, s	p, q, r, s	p, r, t	q, r, s	_						
	20.	p, q, s, t	p, q, r, s, t			-	- 1	Single Corre				
		q, r	1, 1, , , ,	p, q	p, q, s, t	_	-	1. (3)		<b>3.</b> (4)	<b>4.</b> (2)	<b>5.</b> (3)
	21.		q, s	q, s	p, r, s	_	_	<b>6.</b> (4)		<b>8.</b> (3)	<b>9.</b> (2)	<b>10.</b> (2)
	22.	p, q, r, t	p, q, r, s, t	p, q, r, s	p, q, r, s, t		_	<b>11.</b> (3)	<b>12.</b> (4)	<b>13.</b> (2)	<b>14.</b> (2)	<b>15.</b> (1)
	23.	q, r, s, t	p, q, r, t	r, t	r	_	_	Multiple Cor	rect Answ	ers Type		
	24.	ii–p, s	iii–p	iv-q	i–r			1. (2, 4)		<b>2.</b> (1, 2, 4)	3. (	1, 2, 3)
	25.	ii–r	i–q	iv-p	iii–s	iv-r		Linked Comp			<b>3.</b> (.	1, 2, 3)
	26.	ii–p	iii–r	iv–p	i–s	v-q						
	27.	iv–p	i–r	ii–s	iii–q	1	,	<b>1.</b> (1)		<b>3.</b> (1)	<b>4.</b> (2)	<b>5.</b> (4)
	morica	al Value Ty	<b>1</b> 00					Matrix Match	h Type			
			-					1. $(a \rightarrow p,$	$q, s; b \rightarrow$	$p, r, s; c \rightarrow c$	$q, s; d \rightarrow q, s$	)
	1. (4)	<b>2.</b> (3		3) 4	<b>l.</b> (4)	<b>5.</b> (5)		<b>2.</b> (2)			100	
	6. (5)	<b>7.</b> (9	<b>8.</b> (6	5) 9	. (2)	10. (5)		<b>3.</b> (2)				
1	1.(5)	<b>12.</b> (1	14. (4	1) 14	. (2)	<b>15.</b> (2)		<b>4.</b> (3)				
	6. (6, 1)	(	,	3.5) 19		<b>20.</b> (2)		Numerical Va	lue Type			
	1.(2)	<b>22.</b> (5)		<b>24</b>	. (8)	<b>25.</b> (9)				2 (2)	4 (6)	- (2)
14	(1)	25 (2)	• • • • •	`				1.(3)	4. (0)	4 (4)	4 (6)	<b>5</b> (0)

**1.** (3)

**6.** (4)

**2.** (6)

**7.**(1)

**3.** (3)

**8.** (5)

**4.** (6)

**5.** (8)

 $id_{e(s)}$ 

 $^{\mathrm{l}}\mathrm{pl}_{e_{\chi}}$ 

016)

**26.** (1)

31. (4)

**27.** (2)

**32.** (3)

**28.** (8)

**33.** (2)

**29.** (3)

**34.** (1)

**30.** (4)

**35.** (4)

## Qualitative Inorganic Salt Analysis

### **OVERVIEW**

- 1. Analysis of a substance to identify its constituent ions (anions and cations) is known as **qualitative analysis**.
- 2. Determination of the amounts of its component in a given sample is known as **quantitative analysis**.
- 3. Effect of heating of salt (when a gas is evolved)
  - a. Coloured gas:
    - i. Br<sub>2</sub> (Reddish brown) turns starch paper yellow.
       Substance: Bromide

e.g., 
$$2CdBr_2 + O_2 \longrightarrow 2CdO + 2Br_2 \uparrow$$

ii. NO<sub>2</sub> (Brown) turns starch iodine paper blue.

Substance: Nitrites and nitrates of heavy metals

e.g., 
$$2Cu(NO_3)_2 \xrightarrow{\Delta} CuO + 4NO_2 \uparrow + O_2$$

iii. Cl<sub>2</sub> (Greenish yellow) bleach moist litmus paper.

Substance: Chlorides

e.g., 
$$CuCl_2 + H_2O \longrightarrow [CuO + 2HCl] \longrightarrow$$
(Moisture)  $Cu + H_2O + 1/2 Cl_2$ 

iv.  $I_2$  (Violet) turns starch paper blue.

Substance: Iodide

e.g., 
$$2\text{CdI}_2 + \text{O}_2 \longrightarrow 2\text{CdO} + 2\text{I}_2 \uparrow$$

- b. Colourless with odour gas:
  - i. NH<sub>3</sub> Turns red litmus blue.

Ammonium salts

$$(NH_4)_2SO_4 \xrightarrow{\Delta} NH_4HSO_4 + NH_3\uparrow$$

ii. H<sub>2</sub>S – Smell of rotten egg, turns lead acetate paper black sulphides.

$$Na_2S + 2H_2O \xrightarrow{\Delta} 2NaOH + H_2S\uparrow$$

- iii.  $SO_2$  Smell of burning sulphur, turns acidified  $K_2Cr_2O_7$  paper green.
- Sulphites, thiosulphates

$$CaSO_3 \xrightarrow{\Delta} CaO + SO_2$$

iv. HCl – Pungent smell, white fumes with ammonia Hydrated chlorides.

CaCl<sub>2</sub>·6H<sub>2</sub>O 
$$\xrightarrow{\Delta}$$
 Ca(OH)<sub>2</sub> + 4H<sub>2</sub>O + 2HCl $\uparrow$ 

- c. Colourless and odourless gas:
  - i. O<sub>2</sub> Supports glowing.
     Alkali nitrates

$$2KNO_3 \xrightarrow{\Delta} 2KNO_2 + O_2 \uparrow$$

ii.  $CO_2$  – Turns lime water milky.

Carbonates / Oxalates

$$CaCO_3 \xrightarrow{\Delta} CaO + CO_2 \uparrow$$

- 4. Colour change on heating and cooling. (Refer to Section 8.3.1.)
- 5. Substance sublimes and colour of sublimate:

Yellow	As <sub>2</sub> S <sub>3</sub> , HgI <sub>2</sub> turns red on rubbing with glass rod
White	HgCl <sub>2</sub> , Hg <sub>2</sub> Cl <sub>2</sub> , AlCl <sub>3</sub> , As <sub>2</sub> O <sub>3</sub> , Sb <sub>2</sub> O <sub>3</sub>
Blue black or violet	Iodides

6. Substance swells on heating:

Alums, borates, borax and phosphates

7. Substance makes crackling noise on heating:

NaCl, Kl, Pb(NO<sub>3</sub>), Ba(NO<sub>3</sub>),

8. Substance melts on heating:

Salts of alkali metals and salts having water of crystallisation.

- 9. Acid radicals:
  - a. Radicals tested by dilute  $HCVH_2SO_4$ :

Acid radicals	Gas evolved
CO <sub>3</sub> <sup>2-</sup>	$CO_2$
SO <sub>3</sub> <sup>2-</sup>	$SO_2$
S <sup>2-</sup>	H <sub>2</sub> S
NO₂ <sup>⊖</sup>	NO <sub>2</sub> + NO
CH <sub>3</sub> COO <sup>⊖</sup>	CH <sub>3</sub> COOH vapours

### b. Radicals tested by conc. H<sub>2</sub>SO<sub>4</sub>:

Acid radicals	Gas evolved
Cl <sup>⊖</sup>	HCl
Br <sup>⊖</sup>	$HBr + Br_2$
$I_{\Theta}$	$HI + I_2$
NO <sub>3</sub> <sup>⊖</sup>	NO <sub>2</sub>
F <sup>⊝</sup>	HF
C <sub>2</sub> O <sub>4</sub> <sup>2-</sup>	$CO + CO_2$

#### 10. Group of basic radicals and reagents:

Group	Basic radical	Reagent
I	$Ag^{\oplus}, Hg_2^{2+}, Pb^{2+}$	Dil. HCl
IIA	Hg <sup>2+</sup> , Pb <sup>2+</sup> , Cu <sup>2+</sup> , Cd <sup>2+</sup> ,Bi <sup>3+</sup>	Dil. HCl + H <sub>2</sub> S
IIB	As <sup>3+</sup> , Sb <sup>3+</sup> , Sn <sup>2+</sup> , Sn <sup>4+</sup>	Dil. HCl + H <sub>2</sub> S
III	Fe <sup>3+</sup> , Cr <sup>3+</sup> , Al <sup>3+</sup>	NH <sub>4</sub> Cl (Excess) + NH <sub>4</sub> OH
IV	Mn <sup>2+</sup> , Co <sup>2+</sup> , Zn <sup>2+</sup> , Ni <sup>2+</sup>	NH <sub>4</sub> Cl + NH <sub>4</sub> OH + H <sub>2</sub> S
V	Ba <sup>2+</sup> , Sr <sup>2+</sup> , Ca <sup>2+</sup>	NH <sub>4</sub> Cl + NH <sub>4</sub> OH + (NH <sub>4</sub> ) <sub>2</sub> CO <sub>3</sub>
VI	$Mg^{2+}, K^{\oplus}$	NH <sub>4</sub> OH + Na <sub>2</sub> HPO <sub>4</sub>
Zero	NH₄ <sup>⊕</sup>	NaOH

#### 11. Precipitation of group radicals:

a. Group I radicals are precipitated in the form of their chlorides.

AgCl (White), PbCl<sub>2</sub> (White), Hg<sub>2</sub>Cl<sub>2</sub> (White)

**b.** Group II radicals are precipitated in the form of their sulphides.

IIA: HgS(Black)

PbS(Black) CuS(Black)

CdS(Yellow)

Bi<sub>2</sub>S<sub>3</sub>(Black)

**IIB:**  $As_2S_3(Yellow)$   $Sb_2S_3(Orange)$ 

SnS(Brown) SnS<sub>2</sub>(Yellow)

Sulphides of IIA are not soluble but sulphides of IIB are soluble in yellow ammonium sulphide.

c. Group III radicals are precipitated in the form of their hydroxides.

Fe(OH)<sub>3</sub> (Red/Brown)

Cr(OH)<sub>3</sub>(Green/Blue)

Al(OH)<sub>3</sub> (Gelatinous white)

d. Group IV radicals are precipitated in the form of their sulphides.

MnS (Buff)

ZnS (White)

CoS (Black)

NiS (Black)

e. Group V radicals are precipitated in the form of their carbonates.

BaCO<sub>3</sub> (White), SrCO<sub>3</sub> (White), CaCO<sub>3</sub> (White)

Group VI radicals are precipitated in the form of its ammonium phosphate.  $Mg(NH_4)PO_4$  (White)

Group zero: Ammonium salts when heated with NaOH gives off NH<sub>3</sub>.

#### 12. Some important points:

#### a. Effect of heat:

- i. Colour change on heating is due to the change in crystal structure.
- ii. Pb(NO<sub>3</sub>)<sub>2</sub> decomposes with cracking noise  $2Pb(NO_3)_2 \xrightarrow{\Delta} 2PbO + 4NO_2 + O_2$  $2PbCO_3 \xrightarrow{\Delta} 2PbO + CO_2$  $Pb(OH)_2 \cdot 2PbCO_3 \xrightarrow{< 470^{\circ}C} Pb_3O_4 + CO_2 + CO + H_2O_3$  $\stackrel{<}{\longrightarrow}$  3PbO +  $\frac{1}{2}$  O<sub>2</sub> White lead

 $(CH_3COO)_2Pb \xrightarrow{\Delta} CH_3-CO-CH_3+Pb+CO_3$ 

 $CuSO_4.5H_2O \xrightarrow{Exposure} CuSO_4.5H_2O$ 100°C CuSO<sub>4</sub>·4H<sub>2</sub>O Bluish white  $\frac{1}{2} O_2 + SO_2 + CuO \leftarrow CuSO_4$ Black White  $\rightarrow$   $Cu_2O + O_2$ 

iv. Volcano experiment: When orange red monoclinic crystals of ammonium dichromate are heated, it decomposes violently evolving nitrogen and large volumes of green coloured chromium (III) oxide which resembles volcanic ash.

$$(NH_4)_2Cr_2O_7 \longrightarrow Cr_2O_7 + N_2 + 4H_2O$$

This reaction forms the basis of volcano experiment.

v. Reaction of ring test:

$$FeSO_4 + NO \longrightarrow FeSO_4 \cdot NO$$

Nitrosoferrous sulphate (Brown ring)

Note: Oxidation state of NO is +1 in Fe compound, so the oxidation state of Fe in FeSO<sub>4</sub>·NO is +1. It is paramagnetic, its magnetic moment is 3.87 and it is coloured due to the odd electron of NO is fluctuating in between Fe<sup>⊕</sup> and NO. (Charge transfer theory)

$$FeO_4 \cdot 7H_2O + NO \longrightarrow [Fe(H_2O)_5NO]SO_4 + 2H_2O$$
Brown complex

### vi. Evolution of NH, is confirmed by:

A paper soaked in CuSO<sub>4</sub> solution becomes deep blue by NH<sub>3</sub> due to complex formation.

$$(\text{USO}_4 + 4\text{NH}_3 \longrightarrow [\text{Cu(NH}_3)_4]\text{SO}_4$$

$$(\text{Deep blue})$$

$$\text{Hg}_2(\text{NO}_3)_2 + 2\text{NH}_3 \longrightarrow \text{Hg(NH}_2)\text{NO}_3 + \text{Hg} + \text{NH}_4\text{NO}_3$$

vil. All nitrates and nitrites on reduction will give ammonia

$$Zn + 2HCl \longrightarrow ZnCl_2 + 2[H]$$
Lucas reagent

$$NaNO_3 + 8[H] \longrightarrow NH_3 + 2H_2O + NaOH$$

$$NaNO_2 + 6[H] \longrightarrow NH_3 + H_2O + NaOH$$

iji. All nitrates on decomposition give oxygen, metal oxide, NO, except:

$$NH_4NO_3 \xrightarrow{\Delta} N_2O + 2H_2O$$

$$2AgNO_3 \xrightarrow{\Delta} 2Ag + 2NO_2 + O_2$$

$$2NaNO_3 \xrightarrow{\Delta} 2NaNO_2 + O_2$$

ix. All nitrites on decomposition give nitrogen, except

$$N_2H_5NO_2 \xrightarrow{\Delta} N_3H + 2H_2O$$
Hydrazoic acid

v. Some properties of NH2:

$$NH_3 + HCl \longrightarrow NH_4Cl$$

$$2NH_3 + H_2SO_4 \longrightarrow (NH_4)_2SO_4$$

$$NH_3 + HNO_3 \longrightarrow NH_4NO_3$$
.

$$\begin{array}{ccc} Na & O & Cl \\ \hline H & H & \xrightarrow{\Delta} NaCl + H_2O + NH_2. & NH_2. \\ NH_2 & NH_2 & (Hydrazine) \end{array}$$

$$2NH_3 + NaOCl \xrightarrow{\Delta} NaCl + H_2O + NH_2. NH_2$$

(Hydrazine)

$$Na + NH_3 \longrightarrow NaNH_2 + H^{\oplus} + e^{\bigcirc}$$

(solvated 
$$e^{\Theta}$$
 or Ammonated  $e^{\Theta}$ )

$$NaNH_2 + N_2O \longrightarrow N_3H + NaOH \longrightarrow NaN_3 + H_2O$$

$$N_3H + Na_2SO_4$$

xi. Oxidations of ammonia:

$$2NH_3 + 3CaOCl_2 \longrightarrow 3CaCl_2 + N_2 + 3H_2O$$

$$8NH_3 + 3Cl_2 \longrightarrow 6NH_4Cl + N_2$$

$$NH_3 + 3Cl_2 \longrightarrow NCl_3 + HCl$$

(Excess) (Explosive)

$$2NH_3 + 3I_2 \longrightarrow NH_3 \cdot 3HI$$
 (mild explosive)

$$NH_3 + N_2O \longrightarrow NH_4OH$$

xii. Some important reactions:

a. 
$$\text{CuSO}_4 + \text{NH}_4\text{OH} \longrightarrow \text{Cu(OH)}_2 \xrightarrow{\text{NH}_4\text{OH}} \text{[Cu(NH}_3)_4]\text{SO}_4 + \text{H}_2}$$

Light blue

(Blue) Switzer's reagent

$$\Delta + (\text{NH}_4)_2\text{SO}_4$$

CuO

Glucose
$$CuO \xrightarrow{C_6H_{12}O_6} Cu_2O + C_6H_{12}O_7$$
Black
(Red)

Gluconic

**b.** AgCl + NH<sub>4</sub>OH 
$$\longrightarrow$$
 AgOH + NH<sub>4</sub>Cl  $NH_4$ OH (Excess)

$$[Ag(NH_3)_2]Cl + H_2O$$

c. 
$$\text{NiCl}_2 + \text{NH}_4\text{OH} \longrightarrow \text{Ni(OH)}_2 \longrightarrow [\text{Ni(NH}_3)_6]\text{Cl}_2 + \text{H}_2\text{O}$$

**d.** 
$$NH_4OH + HCl \longrightarrow NH_4Cl + H_2O$$

e. 
$$SnCl_4 + 2NH_4Cl \longrightarrow (NH_4)_2 SnCl_6$$
 (Pink salt: used as mordant)

f. 
$$CrCl_3 + 3NH_4OH \longrightarrow Cr(OH)_3 + 3NH_4Cl$$
Green

$$\mathbf{g}. \mathrm{CdSO}_4 + \mathrm{NH}_4\mathrm{OH} \longrightarrow \mathrm{Cd}(\mathrm{OH})_2 \longrightarrow [\mathrm{Cd}(\mathrm{NH}_3)_4]\mathrm{SO}_4 + \mathrm{H}_2\mathrm{O}_4$$

White Soluble complex

**h.** 
$$AlCl_3 + 3NH_4OH \longrightarrow Al(OH)_3 + 3NH_4Cl$$

i. 
$$HgCl_2 + 2NH_4OH \longrightarrow Hg < Cl$$
White

j. 
$$Na_2Cr_2O_7 + 2NH_4OH \longrightarrow (NH_4)_2Cr_2O_7 + 2NaOH$$
Orange
$$Mg_3N_2 \stackrel{Mg^{2+}}{\longleftarrow} N_2 + Cr_2O_3 + H_2O$$
White
$$H_2O$$

$$Mg(OH)_2 + NH_3$$

k. 
$$FeCl_3 + 3NH_4OH \longrightarrow Fe(OH) + 3NH_4Cl$$
Red/Brown

I. Potassium salts give yellow precipitate with sodium cobaltinitrite.

$$Na_3[Co(NO_2)_6] + 3KCl \longrightarrow K_3[Co(NO_2)_6] + 3NaCl$$
(Yellow)

m. Sodium salts give thick white precipitate with potasium dihydrogen antimonate.

$$KH_2SbO_4 + NaCl \longrightarrow NaH_2SbO_4 \downarrow + KCl$$
(White)

### 8.1 INTRODUCTION

Qualitative inorganic analysis is an important part of chemistry. The purpose of this topic is to identify the constituent ions — anions (also called acid radicals) and cations (also called basic radicals). The analysis may be performed by physical, physicochemical and chemical methods. In chemical method of analysis, the constituent ion is usually converted into another compound of known characteristics and the parent ion is thereby inferred.

## 8.2 SYSTEMATIC QUALITATIVE ANALYSIS

Every analysis is divided into three parts:

- 1. The preliminary examination: This includes preliminary examinations such as colour, effect of heating, flame test, borax bead test, charcoal cavity test, cobalt nitrate test, and heating with dilute and concentrated sulphuric acid.
- 2. The examination of anions in solution.
- 3. The examination of cations in solution.

Preliminary examinations are generally useful in the case of simple salt. When a mixture of salts is present in a given sample, the tests generally interfere and give mixed up response. However, heating with dilute and conc. H<sub>2</sub>SO<sub>4</sub> gives indications for the presence of some anions which are confirmed by wet test.

The analysis of basic radicals (cations) is systematic, whereas that of acidic radicals is slightly haphazard.

Acid radicals are analysed first followed by basic radicals, as presence of some acid radicals (known as interfering radicals) creates unwanted problems and therefore their removal become essential at appropriate places.

### 8.2.1 ANALYSIS OF ACID RADICALS (ANIONS)

Systematic identification of anions involves the following steps:

- 1. Preliminary tests with dilute  $H_2SO_4/HCl$ .
- **2.** Preliminary tests with conc.  $H_2SO_4$ .
- **3. Confirmatory test:** Having made a preliminary guess about the presence of anions, confirmation is done by specific tests.
- **4. Tests based on reactions in solution:** Some anions like SO<sub>4</sub><sup>2-</sup>, BO<sub>3</sub><sup>3-</sup>, PO<sub>4</sub><sup>3-</sup>, F<sup>⊖</sup>are tested by their characteristic tests.

### 8.3 PHYSICAL CHARACTERISTICS

**Colour:** Many metallic ions and complex ions have colours and consequently their salts are also coloured. Following table gives the expected constituent of the mixture based on its colour.

Table 8.1 Colour of salts

	.1 Colour of	Suits
S.No.	Colour	Salt
1.	Black	Oxides: MnO <sub>2</sub> , FeO, CuO, Co <sub>3</sub> O <sub>4</sub> ,
	ė	$Ni_2O_3$ , $Fe_3O_4$
		Sulphides: Ag <sub>2</sub> S, CuS, Cu <sub>2</sub> S, FeS, CoS,
		NIS, PbS, HgS, B <sub>12</sub> S <sub>3</sub>
		(blackish brown) powdered metals
2.	Blue	Hydrated CuSO <sub>4</sub> , anhydrous CoSO <sub>4</sub>
3.	Orange	KO <sub>2</sub> , some dichromate (K <sub>2</sub> Cr <sub>2</sub> O <sub>2</sub> ), and
		ferricyanides, Sb <sub>2</sub> S <sub>3</sub>
4.	Green	Nickel salts, hydrated ferrous salts,
		potassium manganate (K <sub>2</sub> MnO <sub>4</sub> ), some
		copper(II), salts, chromium(III) salts
5.	Brownish yellow	SnS
6.	Dark brown	PbO <sub>2</sub> , Ag <sub>2</sub> O, CdO, Fe <sub>2</sub> O <sub>3</sub> , CuCrO <sub>4</sub> , FeCl <sub>3</sub>
		(but yellow in aqueous solution)
7.	Pale brown	MnCO <sub>3</sub>
8.	Purple	Potassium permanganates (KMnO <sub>4</sub> ) and
		a few Cr(III) salts
9.	Light pink	Hydrated manganese salts
10.	Reddish	Hydrated cobalt(II) salts
	pink	
11.	Red	$HgI_2, Pb_3O_4$
12.	Yellow	CdS, PbI <sub>2</sub> , AgBr, AgI, chromates
	A CONTRACTOR OF THE PARTY OF TH	

#### 8.3.1 COLOUR CHANGE ON HEATING

Certain oxides change colour on heating and this fact can be used to identify salt.

Oxides	Colour			
	In cold	On heating		
ZnO	white .	yellow		
SnO <sub>2</sub> , Bi <sub>2</sub> O <sub>3</sub>	yellow	yellowish brown		
$Fe_2O_3$	brown	black/red		
PbO	yellow			

#### 8.3.2 COLOUR OF THE SOLUTION

Colour of the solution	lons suspected
Yellow	CrO <sub>4</sub> <sup>2-</sup> , Fe <sup>3+</sup> , [Fe(CN) <sub>6</sub> ] <sup>4</sup>
Green or blue	Cu <sup>2+</sup> , Ni <sup>2+</sup> , Fe <sup>2+</sup> , Cr <sup>3+</sup>
Pink	Co <sup>2+</sup> , Mn <sup>2+</sup>
Orange or purple	Dichromates (orange), permanganates (purple)

Some salts have their characteristic smell which gives the information. owing information.

Smell	Conclusion
egar or acetic acid type	Acetates (CH <sub>3</sub> COO <sup>⊖</sup> )
mmoniacal smell	Ammonium salts $(NH_4^{\oplus})$

### LUSTRATION 8.1

- FeCl<sub>3</sub> is yellow in aqueous solution but on passing H<sub>2</sub>S gas, solution turns green. Explain.
- Aqueous solution of K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> (orange) changes to yellow. Can you explain?
- Potassium permanganate is purple in colour. On adding KOH, it turns green. What is the compound formed?
- d. A metallic statue under 'acid-rain' attack turns to bluishgreen colour. What can be the probable metal and salt formed?
- e. Oil paintings turn blackish after some time. What is the salt formed? Assume oil paint contains Pb2+.



a. FeCl<sub>3</sub> is yellow in aqueous solution, but on passing H<sub>2</sub>S gas, solution turns green, due to formation of FeCl<sub>2</sub>, which is green in colour.

$$\begin{array}{ccc} \operatorname{FeCl}_3 + \operatorname{H}_2 \operatorname{S} & \longrightarrow & \operatorname{FeCl}_2 + 2\operatorname{HCl} + \operatorname{S} \\ \operatorname{Yellow} & \operatorname{Green} \end{array}$$

**b.** Aqueous solution of potassium dichromate  $(K_2Cr_2O_7)$ changes to yellow due to

$$Cr_2O_7^{2-} + 2OH^{\bigcirc} \Longrightarrow 2CrO_4^{2-} + H_2O$$
Orange

Yellow

c. Potassium permanganate, KMnO<sub>4</sub>, reacts with KOH, producing potassium manganate which is green in

colour.

$$KMnO_4 + KOH \longrightarrow 2K_2MnO_4 + H_2O + \frac{1}{2}O_2$$

Purple Green

**d.** Acid rain constitutes  $HNO_3$  and  $H_2SO_4$ .

HNO<sub>3</sub> on reaction with copper present in statue oxides metallic Cu to Cu<sup>2+</sup>, which gives a bluish-green colour to the statue.

Cu<sub>(s)</sub> + HNO<sub>3(aq)</sub> + 2H<sup>$$\oplus$$</sup><sub>(aq)</sub>  $\longrightarrow$ 

$$Cu^{2+}_{(aq)} + 2NO_2 + 2H_2O$$

Hence metal is Cu and salt formed is Cu<sup>2+</sup>

Oil paintings turn blackish after sometime, due to reaction of Pb2+ (present in oil paints) with sulphides present in atmosphere, which results in the formations of PbS (black in colour)

$$Pb^{2+} + S^{2-} \longrightarrow PbS \downarrow$$
(In oil paint) Black

## 8.4 ANALYSIS OF ANIONS

Though anion analysis is not systematic as cation analysis, the tagorised as:

- 1. First category: The anions which are decomposed by dil. HCl or H<sub>2</sub>SO<sub>4</sub> (5N) are placed in this category. Such anions are  ${\rm CO_3}^{2^{-2}}$ ,  ${\rm CH_3COO}^{\ominus}$ ,  ${\rm S}^{2^{-}}$ ,  ${\rm SO_3}^{2^{-}}$ ,  ${\rm S}_2{\rm O_3}^{2^{-}}$  and  ${\rm NO_2}^{\ominus}$ .
- **2. Second category:** The anions which are decomposed by conc.  $H_2SO_4$  such as  $Cl^{\ominus}$ ,  $Br^{\ominus}$ ,  $I^{\ominus}$ ,  $NO_3^{\ominus}$  and  $F^{\ominus}$ , belong to this category.
- 3. Third category: The anions which are not covered by the first two categories belong to this category. These are usually detected by precipitation reactions, e.g.,

$$SO_4^{2-}$$
,  $C_2O_4^{2-}$ ,  $PO_4^{3-}$  and  $BO_3^{3-}$ .

An anion may interfere with the detection of another anions, in such cases, special tests known as combination test are performed.

Water extracted (W.E.) or sodium carbonate extract (S.C.E.) is used during anion analysis of the mixture.

Preparation of W.E: Small amount (≈ 40-50 mg) of the mixture dissolved in (2-5 mL) of distilled water and boiled for about 1 minute and centrifuge. The centrifugate is called W.E.

Preparation of sodium carbonate extract (S.C.E.): To the small amount ( $\approx$  40-50 mg) of the mixture add ( $\approx$ 200 mg) of Na<sub>2</sub>CO<sub>3</sub> + 5 mL of distilled water and boiled for 5 min and centrifuge. The centrifugate is known as S.C.E. or S.E.

### Advantages of preparing sodium carbonate extract:

- 1. It affords a convenient method for the preparation of a solution of all the anions of the mixture.
- 2. It helps in the removal of cations which could have interfered in the usual tests of some of the anions by converting them into insoluble carbonates. For example, many anions give characteristic precipitates or colours in almost exactly neutral solution which can easily be obtained when the solution is directly prepared from the mixture and contains basic radicals (other than alkali metal ions) as well.
- 3. The residue obtained in preparation of sodium extract may be dissolved in dil. HCl or conc. HCl and the solution so obtained can be used for identification of cations from group I to group VI.

### 8.5 ANALYSIS OF FIRST CATEGORY **ANIONS**

Action of dilute H<sub>2</sub>SO<sub>4</sub>: Treat a small amount of mixture with dil. H<sub>2</sub>SO<sub>4</sub>. Observe the reaction first in cold and then on gentle heating.

S.No.	Observation	Inference
1.	Colourless and odourless gas is evolved with brisk effervescence in cold	CO <sub>3</sub> <sup>2-</sup> may be present
2.	Light brown coloured, pungent fumes evolved in cold which becomes dense on warming	NO <sub>2</sub> <sup>⊖</sup> may be present
3.	Colourless gas is evolved with suffocating odour of burning sulphur	SO <sub>3</sub> <sup>2-</sup> may be present

4.	Colourless gas is evolved with suf- focating odour of burning sulphur on heating and solution turns yel- low	S <sub>2</sub> O <sub>3</sub> <sup>2-</sup> may be present
5.	Colourless gas with smell of rotten eggs is evolved; turns filter paper moistened with lead acetate black	S <sup>2-</sup> may be present
6.	No gas is evolved but the solution smells of vinegar	CH <sub>3</sub> COO <sup>⊖</sup> may be present

## 8.5.1 CONFIRMATORY TESTS FOR ACID RADICALS OR ANIONS

The preliminary tests with dil. H<sub>2</sub>SO<sub>4</sub> and conc. H<sub>2</sub>SO<sub>4</sub> provide useful information regarding presence of many acid radicals. These are confirmed by at least one distinctive confirmatory test. Some of these confirmatory tests are carried out with solution. It is therefore necessary to have a solution containing all (or most) anions free from heavy metal ions. This is best accomplished by preparing sodium carbonate extract.

## 8.5.2 CONFIRMATORY TESTS FOR CARBONATE (CO<sub>3</sub><sup>2-</sup>) ION

S.No.	Experiment	Observation	Inference
1.	Mixture + few drops of dil. H <sub>2</sub> SO <sub>4</sub>	Colourless, odour- less gas with ef- fervescences in cold, increases on heating	CO <sub>3</sub> <sup>2-</sup> may br present
2. a.	Pass the gas evolved through lime water	Lime water turns milky (CaCO <sub>3</sub> )	CO <sub>3</sub> <sup>2-</sup> confirmed
b.	Pass excess of the gas in the lime water	Turbidity disappears giving a clear solution [Ca(HCO <sub>3</sub> ) <sub>2</sub> ]	

#### 8.5.2.1 Chemical Reactions Involved

 Carbonate is decomposed by dil. acids (H<sub>2</sub>SO<sub>4</sub>/HCl) to give CO<sub>2</sub>, a colourless and odourless gas. Evolution of CO<sub>2</sub> is the cause of effervescences.

$$Na_2CO_3 + H_2SO_4 \longrightarrow Na_2SO_4 + CO_2\uparrow + H_2O$$

- 2. On passing the gas evolved (CO<sub>2</sub>) in the above test through lime-water (Ca(OH)<sub>2</sub>, lime water turns milky initially due to the formation of calcium carbonate, CaCO<sub>3</sub>. Excess of CO<sub>2</sub>, when passed through lime water, turbidity disappears and the solution becomes clear due to the conversion of CaCO<sub>3</sub> into Ca(HCO<sub>3</sub>)<sub>2</sub>, (calcium bicarbonate).
  - **a.**  $Ca(OH)_2 + CO_2 \longrightarrow CaCO_3 \downarrow + H_2O$ Lime water Milky
  - **b.**  $CaCO_3 + H_2O + CO_2 \longrightarrow Ca(HCO_3)_2$

### 8.5.3 Tests for Nitrite (NO<sub>2</sub><sup>©</sup>) ION

S.No.	Experiment	Observation	Inference
1.	Mixture + dil. H <sub>2</sub> SO <sub>4</sub> . Heat	Light brown pungent fumes are evolved	NO <sub>2</sub> <sup>⊙</sup> may be present
2.	Bring a paper dipped in KI and starch solution over the mouth of the test tube	Paper turns bluish violet	NO <sub>2</sub> <sup>⊖</sup> confirmed
3.	W.E. + KI solution + starch solution + dil. H <sub>2</sub> SO <sub>4</sub>	Solution turns blue	NO <sub>2</sub> confirmed
4.	W.E. + few drops of sulphanilic acid (in CH <sub>3</sub> COOH) + few drops of α-naphthylamine (in CH <sub>3</sub> COOH)	Red colouration	NO <sub>2</sub> Confirmed
5.	Brown-Ring Test: W.E. + few drops of concentrated soln. of FeSO <sub>4</sub> + a few drops of H <sub>3</sub> SO <sub>4</sub> added from the side of test tube.	Brown ring is formed at the junction of two liquids	NO₂ <sup>Θ</sup> confirmed

#### 8.5.3.1 Chemical Reactions Involved

On reaction with dil. acids (H<sub>2</sub>SO<sub>4</sub>, HCl, CH<sub>3</sub>COOH)
 a nitrite salt decomposes to give nitric oxide, NO. NO
 on reaction with atmospheric O<sub>2</sub> forms brown gas NO<sub>2</sub>.
 (nitrogen dioxide).

2 NaNO<sub>2</sub> + H<sub>2</sub>SO<sub>4</sub> 
$$\xrightarrow{\Delta}$$
 Na<sub>2</sub>SO<sub>4</sub> + 2HNO<sub>2</sub>
dil.

3 HNO<sub>2</sub>  $\longrightarrow$  H<sub>2</sub>O + HNO<sub>3</sub> + 2NO
Colourless

2 NO + O<sub>2</sub>  $\longrightarrow$  2NO<sub>2</sub>↑
Air Brown gas

2. NO<sub>2</sub> produced in above test, reacts with KI, which results in the liberation of I<sub>2</sub> gas. I<sub>2</sub> on reaction with starch forms starch-I<sub>2</sub> adsorption complex which is bluish violet in colour.

$$2 \text{ NO}_2 + \text{KI} \longrightarrow 2 \text{NO}_2 + \text{I}_2 \uparrow$$
 $I_2 + \text{Starch} \longrightarrow \text{Starch} - I_2 \text{ adsorption complex}$ 
(Bluish violet colour)

- **3.** Same reactions as for test 2.
- 4. Sulphanilic acid and  $\alpha$ -naphthylamine are dissolved in separate test tubes in CH<sub>3</sub>COOH. These are then added to the water extract, resulting in the formation of red coloured dye.

5. Brown ring test: To the water extract, freshly prepared FeSO<sub>4</sub> solution is added. Dilute H<sub>2</sub>SO<sub>4</sub> is added from the side of the test tube, a brown ring is formed at the junction of the two liquids. Brown ring is due to the formation of  $[Fe(H_2O)_5(NO)]SO_4$ .

$$2 \text{ NaNO}_2 + \text{H}_2 \text{SO}_4 \longrightarrow \text{Na}_2 \text{SO}_4 + 2 \text{ HNO}_2$$

$$3 \text{ HNO}_2 \longrightarrow \text{ HNO}_3 + \text{H}_2 \text{O} + \text{NO}$$

$$[\text{Fe}(\text{H}_2 \text{O})_6] \text{SO}_4 + \text{NO} \longrightarrow [\text{Fe}^{\oplus}(\text{H}_2 \text{O})_5 (\text{NO}^{\oplus})] \text{SO}_4 + \text{H}_2 \text{O}$$

$$\text{Brown ring}$$

Brown ring complex is paramagnetic with 3 unpaired electrons.

Note: This test should not be performed for nitrate in presence of nitrite, bromide and iodide.

### 8.5.4 TESTS FOR SULPHITE (SO<sub>3</sub><sup>2-</sup>) ION

S. No.	Experiment	Observation	Inference
1.	Mixture + few drops of dil.H <sub>2</sub> SO <sub>4</sub> .Heat	Colourless gas with pungent and suf- focating odour of burning sulphur	SO <sub>3</sub> <sup>2-</sup> may be present
2.	Bring a filter paper moistened with soln of K <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub> acidified with dil. H <sub>2</sub> SO <sub>4</sub> over the liberated gas	The colour of the paper turns green	SO <sub>3</sub> <sup>2-</sup> confirmed
3. i.	S.C.E. + dil.HCl (till acidic) + BaCl <sub>2</sub> solution	White ppt. (BaSO <sub>3</sub> ) which is soluble in conc. HCl	SO <sub>3</sub> <sup>2-</sup> confirmed
ii.	Add Br <sub>2</sub> water to the above solution	White ppt (BaSO <sub>4</sub> ) insoluble in conc. HCl	SO <sub>3</sub> <sup>2-</sup> confirmed

### 8.5.4.1 Chemical Reactions Involved

1. Sulphites are decomposed by dilute acids to give sulphur dioxide gas, SO<sub>2</sub> which is a colourless gas with pungent and suffocating smell of burning sulphur.

focating smell of burning surprior.  

$$Na_2SO_3 + H_2SO_4 \xrightarrow{\Delta} Na_2SO_4 + H_2O + SO_2 \uparrow$$

$$SO_3^{2-} + 2H^{\oplus} \longrightarrow SO_2^{\uparrow} + H_2O$$

2. K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>, in acidic medium behaves as an oxidising agent, whereas SO<sub>2</sub> behaves as reducing agent. SO<sub>2</sub> when comes in contact with acidified K2Cr2O7 reduces it to Cr2(SO4)3, which is green in colour.

$$Cr_2O_7^{2-} + 14H^{\oplus} + 6e^{\Theta} \longrightarrow 2Cr^{3+} + 7H_2O$$

$$[SO_2 + 2H_2O \longrightarrow SO_4^{2-} + 4H^{\oplus} + 2e^{\Theta}] \times 3$$

$$Cr_2O_7^{2-} + 2H^{\oplus} + 3SO_2 \longrightarrow 2Cr^{3+} + H_2O + 3SO_4^{2-}$$

$$(Green)$$
or  $K_2Cr_2O_7 + 4H_2SO_4 + 3SO_2 \longrightarrow K_2SO_4 + Cr_2(SO_4)_3 + H_2O$ 

$$(Green)$$

3. S.C.E. acidified with dil. HCl and then BaCl<sub>2</sub> solution is added, formation of white precipitate soluble in conc. HCl confirms the presence of sulphite ions

$$Na_2SO_3 + HCl + BaCl_2 \longrightarrow NaCl + H_2O + BaSO_3 \downarrow$$
  
On addition of  $Br_2$  water to the above solution, white precipitate of  $BaSO_4$  insoluble in conc. HCl is obtained. Since  $Br_2$ , which is an oxidising agent, oxidises  $SO_3^{2-}$  to  $SO_4^{2-}$  (sulphate ion).  
 $BaSO_3 \xrightarrow{Br_2 \text{ water}} BaSO_4 \downarrow$ 

### 8.5.5 TESTS FOR THIOSULPHATE (S<sub>2</sub>O<sub>3</sub><sup>2-</sup>) ION

S.No.	Experiment	Observation	Inference
1.	Mixture + dil. H <sub>2</sub> SO <sub>4</sub> . Heat	Colourless gas with suffocating odour of burning sulphur. SO <sub>2</sub> is evolved and solution turns yellow (S)	S <sub>2</sub> O <sub>3</sub> <sup>2-</sup> may be present
2.	Bring a paper moistened with acidified solution of $K_2Cr_2O_7$ over the ensuing gas	Colour of the paper turns green	S <sub>2</sub> O <sub>3</sub> <sup>2-</sup> confirmed
3.	S.C.E. + AgNO <sub>3</sub> solution	White ppt. quickly changing to yellow brown and finally black (Ag <sub>2</sub> S)	S <sub>2</sub> O <sub>3</sub> <sup>2-</sup> confirmed
4.	S.C.E. + few drops of I <sub>2</sub> solution	Colour of I <sub>2</sub> is discharged	S <sub>2</sub> O <sub>3</sub> <sup>2-</sup> confirmed

#### 8.5.5.1 Chemical Reactions Involved

1. Thiosulphates are decomposed by dil. acids on heating resulting in the evolution of SO2, a colourless gas, with suffocating odour of burning sulphur and solution turns yellow because of formation of sulphur.

$$Na_2S_2O_3 + H_2SO_4 \xrightarrow{\Delta} Na_2SO_4 + H_2O + SO_2\uparrow + S\downarrow$$
dil.

- 2. Same reaction as for test 2 for sulphite ion.
- 3. On addition of AgNO<sub>3</sub> solution to S.C.E. a white precipitate (Ag<sub>2</sub>S<sub>2</sub>O<sub>3</sub>) is formed which quickly changes to black (Ag<sub>2</sub>S)



$$\begin{array}{c} \text{S}_2\text{O}_3^{2-} + 2\text{Ag}^{\oplus} \longrightarrow \text{Ag}_2\text{S}_2\text{O}_3 \downarrow \\ \text{White precipitate} \\ \text{Ag}_2\text{S}_2\text{O}_3 + \text{H}_2\text{O} \longrightarrow \text{Ag}_2\text{S} \downarrow + \text{H}_2\text{SO}_4 \end{array}$$

**4.** On addition of  $I_2$  solution to S.C.E. colour of  $I_2$  disappears as  $I_2$  is reduced to  $I^{\Theta}$  (iodide ion)  $2S_2O_3^{2-} + I_2 \longrightarrow 2I^{\Theta} + S_4O_6^{2-}$ 

### 8.5.6 TESTS FOR SULPHIDE (S<sup>2-</sup>) ION

S.No.	Experiment	Observation	Inference
1.	Mixture + few drops of dil. H <sub>2</sub> SO <sub>4</sub>	Colourless gas with rotten egg smell (H <sub>2</sub> S) is evolved on heating	S <sup>2-</sup> may be present
2.	S.C.E. + dil. H <sub>2</sub> SO <sub>4</sub> (to acidify) + lead acetate solution	Black ppt. (PbS)	S <sup>2-</sup> confirmed
3.	S.C.E. + dil. H <sub>2</sub> SO <sub>4</sub> (to acidify) + CdCO <sub>3</sub> solution	Yellow ppt. (CdS)	S <sup>2-</sup> confirmed
4.	S.C.E. + alkaline solution of sodium nitroprusside	Violet colour	S <sup>2-</sup> confirmed

#### 8.5.6.1 Chemical Reactions Involved

1. Dilute acids decompose sulphide salts on heating to form H<sub>2</sub>S gas which is a colourless gas and has rotten egg smell.

$$Na_2S + H_2SO_4 \xrightarrow{\Delta} H_2S\uparrow + Na_2SO_4$$
dil.

or 
$$(S^{2-} + 2H^{\oplus} \longrightarrow H_2S \uparrow)$$

2. Lead acetate, Pb(CH<sub>3</sub>COO)<sub>2</sub> soln. turns black on reacting with H<sub>2</sub>S gas due to the formation of lead sulphide,

$$Pb(CH_3COO)_2 + H_2S \longrightarrow PbS \downarrow + 2CH_3COOH$$
Black

or 
$$(Pb^{2+} + S^{2-} \longrightarrow PbS)$$

**3.** Yellow precipitate of CdS is formed when sodium extract reacts with CdCO<sub>3</sub>.

$$H_2S + CdCO_3 \longrightarrow CdS \downarrow + H_2O + CO_2$$

Yellow

or 
$$(S^{2-} + Cd^{2+} \longrightarrow CdS \downarrow)$$

**4.** On addition to alkaline solution of sodium nitroprusside to S.C.E., violet colouration is obtained.

$$Na_2S + Na_2^{2+} [Fe^{2+} (CN^{-5})_5 (NO^{\oplus})]^{2-}$$

Sodium nitroprusside

$$\longrightarrow Na_4^{+4} [Fe^{2+} (CN^{-5})_5 NO^{\Theta} S]^{4-}$$

or 
$$(S^{2-} + [Fe(CN)_5 \overset{\oplus}{NO}]^{2-} \longrightarrow [Fe(CN)_5 (\overset{\ominus}{NOS})]^{4-}$$

### 8.5.7 Tests for Acetate (CH<sub>3</sub>COO<sup>⊙</sup>) ION

S.No.	Experiment	Observation		
3.140.	Experiment		Inference	
1.	Mixture + few drops of dil. H <sub>2</sub> SO <sub>4</sub> .Heat	Smell of vinegar is observed without evolution of any gas	CH <sub>3</sub> COO <sup>©</sup> may be present	
2.	W.E. + neutral FeCl <sub>3</sub> solution	Blood red colouration [Fe(CH <sub>3</sub> COO) <sub>3</sub> ]	CHCOO <sup>⊖</sup> confirmed	
3.	Mixture + 1 mL $C_2H_5OH + 5-6$ drops of conc. $H_2SO_4$ . Warm for about 10 min. Transfer the above solution in a beaker containing about 100 ml of water.	Pleasant fruity odour	CHCOO <sup>©</sup> confirmed	

### 8.5.7.1 Chemical Reactions Involved

1. Dilute acids on reaction with acetates, form acetic acid which has a smell of vinegar.

$$Pb(CH_3COO)_2 + H_2SO_4 \xrightarrow{\Delta} PbSO_4 \downarrow + 2CH_3COOH$$
  
 $dil.$   
or  $(Pb^{2+} + SO_4^{2-} \longrightarrow PbSO_4 \downarrow)$ 

2. W.E. on reacting with neutral FeCl<sub>3</sub> solution gives blood-red colouration due to formation of ferric acetate, [Fe(CH<sub>3</sub>COO)<sub>3</sub>]

$$3\text{CH}_3\text{COO}^{\odot} + \text{Fe}^{3+} \longrightarrow [\text{Fe}(\text{CH}_3\text{COO})_3]$$
(Neutral) Blood-red colour

**Note:** In the FeCl<sub>3</sub> test for acetates, the solution must be neutral and must not contain anions which precipitate ferric ions:  $CO_3^{2-}$ ,  $SO_3^{2-}$ ,  $PO_4^{3-}$ ,  $I^{\Theta}$  etc.  $I^{\Theta}$  is oxidised to  $I_2$  by Fe<sup>3+</sup> ion, which produces a reddish brown colour similar to that expected in the reaction.

3. On treatment of the mixture with ethanol (C<sub>2</sub>H<sub>5</sub>OH) and conc. H<sub>2</sub>SO<sub>4</sub>, pleasant fruity smell is obtained due to formation of ethylacetoacetate (CH<sub>3</sub>COOC<sub>2</sub>H<sub>5</sub>)

$$2CH_3COONa + H_2SO_4 \longrightarrow 2CH_3COOH + Na_2SO_4$$
  
 $CH_3COOH + C_2H_5OH \longrightarrow CH_3COOC_3H_5 + H_3O$ 

#### ILLUSTRATION 8.2

a. Identify (A), (B) and (C).

A + dil.  $H_2SO_4 \longrightarrow$  brown colour vapours turning (KI + starch) paper blue.

 $A + NaOH \xrightarrow{\Delta} NH_3$  gas

(A)  $\xrightarrow{\Delta}$  (B) (gas) + (C) (gas, but liquid at room temperature)

- **b.** CO<sub>2</sub> and SO<sub>2</sub> both turn lime water milky. How will you detect the presence if both are present in a mixture?
- c. (A),  $(M_2X \cdot 7H_2O)$  has water and  $M_2X$  (M is monovalent alkaline cation, and X is any divalent anion) in 1:1 ratio by weight. (A) on reaction with dil. $H_2SO_4$  gives a gas that turns  $K_2Cr_2O_7/H^{\oplus}$  solution green. Identify (A) and explain reactions.

(A), (Black) + dil.  $H_2SO_4 \longrightarrow (B)$  (gas) + (C) (light green colour solution). Gas (B) turns lead acetate paper black. What are (A), (B) and (C)?

g. (A): NH<sub>4</sub>NO<sub>2</sub>

 $(B): N_2$ 

(C): H,O

b. pass the mixture of gases first into acidified K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> solution then into lime water.

 $_{1f}K_{2}Cr_{2}O_{7}$  solution turns green –  $SO_{2}$ If lime water turns milk - CO,

<sub>c. (A)</sub>: Na<sub>2</sub>SO<sub>3</sub>·7H<sub>2</sub>O

d. (A): FeS

 $(B): H_{2}S$ 

(C): FeSO<sub>4</sub>

### 8.6 ANALYSIS OF SECOND CATEGORY ANIONS

action of conc. H2SO4: Treat a small amount of mixture with H,SO<sub>4</sub>. Observe the reaction first in cold and then on gentle heating.

S.No.	Observation	Inference
1.	Colourless gas with pungent odour is evolved; gives white fumes when a glass rod dipped in NH <sub>4</sub> OH is brought over it	Cl <sup>©</sup> may be present
2.	Evolution of light reddish brown coloured gas with a pungent odour; gives a fumes when a rod dipped in NH <sub>4</sub> OH is brought over it	Br <sup>©</sup> may be present
3.	Evolution of violet fumes with pungent odour	I <sup>⊙</sup> may be present
4.	Light brown coloured gas with pungent odour is evolved, colour deepens on addition of Cu turnings	NO <sub>3</sub> <sup>⊖</sup> may be present
5.	Colourless, odourless gas is evolved, turns lime-water milky	C <sub>2</sub> O <sub>4</sub> <sup>2-</sup> may be present

### 8.6.1 TESTS FOR CHLORIDE (CI<sup>©</sup>) ION

Experiment	Observation	Inference
Mixture + few drops of conc.	Colourless gas with pungent smell (HCl)	Cl <sup>⊕</sup> may be present
Bring a glass rod dipped in NH <sub>4</sub> OH near the mouth of the test tube	White dense fumes are formed	Cl <sup>⊖</sup> may be present
Add MnO <sub>2</sub> in the same test tube	Pale green gas (Cl <sub>2</sub> )	, , ,
S.C.E. and heat + dil. HNO <sub>3</sub> (to acidity) + AgNO <sub>3</sub> solution	White ppt. soluble in NH <sub>4</sub> OH. White ppt. reappears on adding dil. HNO <sub>3</sub>	Cl <sup>O</sup> confirmed
	drops of conc.  H <sub>2</sub> SO <sub>4</sub> .Heat  Bring a glass rod dipped in NH <sub>4</sub> OH near the mouth of the test tube  Add MnO <sub>2</sub> in the same test tube  S.C.E. and heat + dil.  HNO <sub>3</sub> (to acidity) +	Mixture + few drops of conc.  H <sub>2</sub> SO <sub>4</sub> .Heat  Bring a glass rod dipped in NH <sub>4</sub> OH near the mouth of the test tube  Add MnO <sub>2</sub> in the same test tube  S.C.E. and heat + dil. HNO <sub>3</sub> (to acidity) + AgNO <sub>2</sub> solution  Colourless gas with pungent smell (HCl)  White dense fumes are formed  Pale green gas (Cl <sub>2</sub> )  White ppt. soluble in NH <sub>4</sub> OH. White ppt. reappears on

<b>i.</b>	In a dry test tube, take the mixture + K <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub> solid (twice the amount of mixture + conc.	Deep orange red vapours of chromyl chloride (CrO <sub>2</sub> Cl <sub>2</sub> )	
ii.	H <sub>2</sub> SO <sub>4</sub> .Heat  Pass the vapours from (i) in 5%  NaOH solution in a test tube	Colour of NaOH solution changes to yellow	
iii.	Yellow solution from (i) + CH <sub>3</sub> COOH dropwise till acidic + lead acetate solution	Yellow precipitate	Cl <sup>©</sup> confirmed

Note: 1. Bromides and iodides do not interfere with the chromyl chloride (CrO<sub>2</sub>Cl<sub>2</sub>) test, because they are oxidised to Br<sub>2</sub> (red vapours) and I<sub>2</sub> (violet vapours) which dissolve in the NaOH solution to form colourless products (halide + hypohalite/halate).

$$Br_{2} + 2OH^{\bigcirc} \longrightarrow Br^{\bigcirc} + BrO^{\bigcirc} + H_{2}O \text{ (cold)}$$

$$3Br_{2} + 6OH^{\bigcirc} \longrightarrow \underbrace{5Br^{\bigcirc} + BrO_{3}^{\bigcirc} + 3H_{2}O}_{\text{(Colourless)}} \text{ (hot)}$$

2. Hg<sub>2</sub>Cl<sub>2</sub> and HgCl<sub>2</sub> do not respond to the chromyl chloride test because they are ionised to a very small extent. This test fails in case of chlorides of Pb, Ag, Sb and Sn only partially form CrO<sub>2</sub>Cl<sub>2</sub> in the reaction.

#### 8.6.1.1 Chemical Reactions Involved

1. On heating with conc. H<sub>2</sub>SO<sub>4</sub>, a chloride salt is decomposed to give a colourless gas HCl with pungent smell.

$$KC1 + H_2SO_4 \xrightarrow{\Delta} KHSO_4 + HC1\uparrow$$
conc.

2. a. HCl gas evolved in the above step, when comes in contact with NH<sub>4</sub>OH, results in the formation of dense white fumes due to formation of NH<sub>4</sub>Cl

$$NH_4OH + HCl \longrightarrow NH_4Cl \uparrow + \dot{H}_2O$$

**b.** (MnO<sub>2</sub>) manganese dioxide oxidises HCl to Cl<sub>2</sub>, a pale green gas.

$$4HCl + MnO_2 \xrightarrow{\Delta} MnCl_2 + Cl_2 \uparrow + 2H_2O$$

3. On addition of AgNO<sub>3</sub> solution, to the chloride salt, a white precipitate of AgCl is formed. AgCl is soluble in NH<sub>4</sub>OH due to formation of complex [Ag(NH<sub>3</sub>)<sub>2</sub>]Cl. which decomposes on addition of HNO<sub>3</sub>.

$$\begin{array}{c} \text{KCl} + \text{AgNO}_{3} \longrightarrow \text{AgCl} \downarrow + \text{KNO}_{3} \\ \text{White} \\ \text{AgCl} + \text{NH}_{4}\text{OH} \longrightarrow [\text{Ag(NH}_{3})_{2}]\text{Cl} + \text{H}_{2}\text{O} \\ \text{Soluble} \\ [\text{Ag(NH}_{3})_{2}]\text{Cl} + 2\text{HNO}_{3} \longrightarrow \text{AgCl} \downarrow + 2\text{NH}_{4}\text{NO}_{3} \\ \text{White} \end{array}$$

### **4. Chromylchloride test** (not for $Br^{\Theta}/I^{\Theta}$ ions)

**a.** On addition of cone. H<sub>2</sub>SO<sub>4</sub> and K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> (potassium dichromate) to chloride salt, deep orange red vapours of chromyl chloride, CrO<sub>2</sub>Cl<sub>2</sub>, are produced.

$$KC1 + H_2SO_4 \xrightarrow{\Delta} KHSO_4 + HC1$$

$$K_2Cr_2O_7 + 2H_2SO_4 \longrightarrow 2KHSO_4 + 2CrO_3 + H_2O$$

$$cone.$$

$$2HC1 + CrO_3 \longrightarrow CrO_2Cl_2 \uparrow + H_2O$$

$$Chromyl$$

$$chloride$$

**b.** Colour of NaOH solution changes to yellow, when chromyl chloride vapours are passed through it due to the formation of Na<sub>2</sub>CrO<sub>4</sub> (sodium chromate).

$$CrO_2Cl_2 + 4NaOH \longrightarrow Na_2CrO_4 + 2NaCl + 2H_2O$$
Yellow

c. On addition of lead acetate, Pb(CH<sub>3</sub>COO)<sub>2</sub> to the above solution, yellow precipitate of PbCrO<sub>4</sub> (lead chromate) is formed.

$$Na_2CrO_4 + Pb(CH_3COO)_2 \longrightarrow PbCrO_4 \downarrow + 2CH_3OONa$$
Yellow

### 8.6.2 Tests for Bromide (Br<sup>©</sup>) Ion

S.No.	Experiment	Observation	Inference
1.	Mixture + few drops of conc. H <sub>2</sub> SO <sub>4</sub> . Heat	Reddish brown pungent gas (Br <sub>2</sub> ) is evolved	Br <sup>⊖</sup> may be present
2.	In the above solution add MnO <sub>2</sub> solid. Heat	Gas becomes denser	Br <sup>⊖</sup> may be present
3.	S.E. + dil. HNO <sub>3</sub> (to acidify) + AgNO <sub>3</sub> solution	Light yellow precipitate sparingly soluble in NH <sub>4</sub> OH (dil.) but soluble in conc. NH <sub>3</sub>	Br <sup>⊖</sup> confirmed
4.	Layer test: S.E. + CCl <sub>4</sub> / CHCl <sub>3</sub> + Cl <sub>2</sub> wa- ter. Shake vigor- ously	The organic solvent layer turns brown	Br <sup>⊖</sup> confirmed

### 8.6.2.1 Chemical Reactions Involved

1. On heating bromide salt on reaction with conc. H<sub>2</sub>SO<sub>4</sub> is decomposed to give a reddish brown gas (Br<sub>2</sub>) with pungent smell.

$$KBr + H_2SO_4 \xrightarrow{\Delta} KHSO_4 + HBr$$

$$conc.$$

$$2HBr + H_2SO_4 \xrightarrow{\Delta} Br_2 \uparrow + 2H_2O + SO_2$$

$$(Reddish$$
brown gas)

2. Addition of MnO<sub>2</sub> to the above solution results in oxidation of HBr to Br<sub>2</sub>, resulting in intensification of reddish brown fumes.

$$4HBr + MnO_2 \xrightarrow{\Delta} Br_2 + 2H_2O + MnBr_2$$

3. Addition of AgNO<sub>3</sub> solution to the acidified sodium carbonate extract results in formation of light yellow precipitate of AgBr which is sparingly soluble in NH<sub>4</sub>OH.

NaBr + AgNO<sub>3</sub> → AgBr ↓ + NaNO<sub>3</sub>

AgBr + NH<sub>4</sub>OH → [Ag(NH<sub>3</sub>)<sub>2</sub>]Br + H<sub>2</sub>O

**4. Layer test:** Bromine (Br<sub>2</sub>) is liberated from bromide salt on addition of an oxidising agent (Cl<sub>2</sub> water/drop of KMnO<sub>4</sub> solution/conc. HNO<sub>3</sub>). Br<sub>2</sub> being more soluble in organic medium (CCl<sub>4</sub>/CHCl<sub>3</sub>) gives an orange brown colour to the lower organic layer and the upper aqueous layer remains colourless.

$$2Br^{\Theta} + Cl_2 \longrightarrow 2Cl^{\Theta} + Br_2 \uparrow$$

### 8.6.3 Tests for lodide (I<sup>©</sup>) Ion

S.No.	Experiment	Observation	Inference
1.	Mixture + few drops of conc. H <sub>2</sub> SO <sub>4</sub> . Heat	Violet coloured pungent fumes are evolved	I <sup>©</sup> may be present
2.	Above solution + MnO <sub>2</sub> (s). Heat	Fumes becomes denser	I <sup>⊕</sup> may be present
3.	S.E. + dil. HNO <sub>3</sub> (till acidic) + AgNO <sub>3</sub> solution	Yellow precipitate insoluble in NH <sub>4</sub> OH	I <sup>⊖</sup> confirmed
4. i.	Layer test: S.E. + CCl <sub>4</sub> (or CHCl <sub>3</sub> or CS <sub>2</sub> ) + Cl <sub>2</sub> water. Shake vigorously	Organic solvent layer turns violet	[ <sup>⊖</sup> confirmed
ii.	In the solution (4) add excess of Cl <sub>2</sub> water	Organic solvent layer becomes colourless	I <sup>⊕</sup> confirmed

### 8.6.3.1 Chemical Reactions Involved

1. Iodides are decomposed by conc. H<sub>2</sub>SO<sub>4</sub> on heating to liberate violet fumes.

$$KI + H_2SO_4 \xrightarrow{\Delta} HI + KHSO_4$$
  
 $HI + H_2SO_4 \longrightarrow I_2 \uparrow + 2 H_2O + SO_2$ 

**2.** On addition of  $MnO_2$ , to the above mixture, only  $I_2$  is evolved.

$$MnO_2 + HI \xrightarrow{\Delta} I_1 \uparrow + 2H_1O + MnI_1$$

3. Addition of AgNO<sub>3</sub> solution to the acidified sodium carbonate results in the formation of yellow precipitate (AgI), which is insoluble in NH<sub>4</sub>OH.

$$NaI + AgNO_3 \longrightarrow AgI \downarrow + NaNO_3$$

**4. Layer test:** Addition of Cl<sub>2</sub> water, an oxidising agent to the sodium extract, results in the liberation of I<sub>2</sub> from iodide, which gives violet colour to the organic layer. On excess addition of Cl<sub>2</sub> water, the organic layer becomes colourless due formation of iodic acid, HIO<sub>3</sub>

$$2I^{\Theta} + Cl_2 \longrightarrow 2Cl^{\Theta} + I_2^{\uparrow}$$

Violet

$$5Cl_2 + I_2 + 6H_2O \longrightarrow 2HIO_3 + 10HCl$$
Colourless

## 16.4 TESTS FOR NITRATE (NO3°) ION

Experiment	Observation	Inference
Mixture + few drops of conc. H <sub>2</sub> SO <sub>4</sub>	Reddish brown fumes (NO <sub>2</sub> ) with pungent odour are evolved	NO <sub>3</sub> <sup>⊖</sup> may be present
Mixture (i) + Cu turnings. Heat	Fumes becomes denser	NO <sub>3</sub> <sup>⊖</sup> may be present
Ring test: S.E. + dil. HCl (till acidic) + freshly prepared solution of FeSO <sub>4</sub> + few drops of conc. H <sub>2</sub> SO <sub>4</sub> gradually from the side of the test tube without disturbing the liquids in the test tube.	Brown ring is formed at the junction of the two liquids	NO <sub>3</sub> ⊖ confirmed

Note: Bromide and iodides interfere in this test because of liherated halogens. Nitrites give similar test as nitrates.

4. S.E met Boi few of I	. + a piece of Zn ral + dil. H <sub>2</sub> SO <sub>4</sub> . I for 5 min. Add drops each KI and starch	Violet colouration	NO <sub>3</sub> confirmed
S.E till dro aci of am	e test: 2. + CH <sub>3</sub> COOH acidic + few ops of sulphanilic d + few drops α-naphthyl ine + Zn dust (in H <sub>3</sub> COOH)	Red colouration	NO <sub>3</sub> <sup>⊖</sup> confirmed

Note: Nitrites give similar test but without adding Zn dust.

### 8.6.4.1 Chemical Reactions Involved

1. Reddish brown vapours of nitrogen dioxide (NO<sub>2</sub>) accompanied by pungent acid vapours of nitric acid (HNO<sub>3</sub>), which fumes in the air, are formed on heating nitrate salt with conc. H<sub>2</sub>SO<sub>4</sub>.

with conc. 
$$H_2SO_4$$
.  
 $NaNO_3 + H_2SO_4 \xrightarrow{\triangle} NaHSO_4 + HNO_3$ 

$$4\text{HNO}_3 \xrightarrow{\text{conc.}} 4\text{NO}_2 \uparrow + O_2 + 2\text{H}_2\text{O}$$
Reddish brown fumes
$$\text{Reddish brown fumes}$$
Reddish brown fumes

2. On heating the nitrate salt with conc.  $H_2SO_4$  and copper turnings, reddish brown fumes become denser and the solution acquires a blue colour due to the production of cupric nitrate Cu(NO<sub>3</sub>)<sub>2</sub>.

 $3C_{11} + 91D_{10} = \Delta 3C_{10}(NO_{2})_{2} + 2NO + 4H_{2}O$ 

$$2NO + O_2 \longrightarrow 2NO_2 \uparrow$$

3. Ring test: This test is carried out by the addition of freshly prepared solution of FeSO<sub>4</sub> to the nitrate solution, followed by slow addition of conc. H<sub>2</sub>SO<sub>4</sub> from the side of the test tube so that the acid forms a layer beneath the mixture. A brown ring will be formed where the liquids meet or at the junction of the two liquids. Brown ring is formed due to the complex [Fe(H<sub>2</sub>O)<sub>5</sub>(NO)]SO<sub>4</sub>

$$NaNO_3 + H_2SO_4 \longrightarrow NaHSO_4 + HNO_3$$
  
conc.

$$6 \text{FeSO}_4 + 2 \text{HNO}_3 + 3 \text{H}_2 \text{SO}_4 \longrightarrow 3 \text{Fe}_2 (\text{SO}_4)_3 + 2 \text{NO} + 4 \text{H}_2 \text{O}$$

$$[\text{Fe}(\text{H}_2 \text{O})_6] \text{SO}_4 + \text{NO} \longrightarrow [\text{Fe}^{\oplus} (\text{H}_2 \text{O})_5 (\text{NO})^{\oplus}]^{2+} \text{SO}_4^{-2} \cdot \text{H}_2 \text{O}$$
Brown ring

The brown complex contains 3 unpaired electrons and is paramagnetic with  $\mu = \sqrt{3(3+2)} = \sqrt{15}$  B.M.

4. Boil S.E. with Zn dust and dil. H<sub>2</sub>SO<sub>4</sub>. Add KI and starch solution, violet colouration is observed. Zinc dust in presence of H<sub>2</sub>SO<sub>4</sub> acts as reducing agent, by liberating nascent hydrogen. Nitrates are being reduced to nitrite.

$$Zn + H_2SO_4 \longrightarrow ZnSO_4 + 2 [H]$$

$$NaNO_3 + 2[H] \longrightarrow NaNO_2 + H_2O$$

$$2NaNO_2 + H_2SO_4 \longrightarrow Na_2SO_4 + 2HNO_2$$

$$3HNO_2 \longrightarrow H_2O + HNO_3 + 2NO$$

$$Colourless$$

$$2NO + O_2 \longrightarrow 2NO_2 \uparrow$$

$$Brown gas$$

$$2NO_2 + 2 KI \longrightarrow 2KNO_2 + I_2 \uparrow$$

$$I_2 + Starch \longrightarrow Starch - I_2 adsorption complex$$

$$Violet$$

5. Dye test: To the nitrates,  $\alpha$ -naphthylamine solution (in CH<sub>3</sub>COOH), sulphanilic acid (in CH<sub>3</sub>COOH) and zinc dust are added. Red coloured solution is obtained. Zinc dust reduces nitrates to nitrites, which further reacts to form red colour azo dye.

RO<sub>3</sub><sup>©</sup> + Zn (dust) 
$$\longrightarrow$$
 NO<sub>2</sub><sup>©</sup>

HO<sub>3</sub>S  $\longrightarrow$  NH<sub>2</sub> + H<sup>®</sup> + NO<sub>2</sub><sup>©</sup> + CH<sub>3</sub>COOH

Sulphilinic acid

HO<sub>3</sub>S  $\longrightarrow$  N=N-OOC-CH<sub>3</sub> + 2H<sub>2</sub>O

NH<sub>2</sub> ( $\alpha$ -napthylamine)

HO<sub>3</sub>S  $\longrightarrow$  N=N  $\longrightarrow$  NH<sub>2</sub> + CH<sub>3</sub>COOH

### 8.6.5 Tests for Oxalate $(C_2O_4^{2-})$ Ion

S.No.	Experiment	Observation	Inference
1.	Mixture + conc. H <sub>2</sub> SO <sub>4</sub> . Heat	Colourless, odourless gas evolved	
2.	Bring the mouth of the test tube near the flame and take it off	The gas burns with a blue flame at the mouth of the test tube	C <sub>2</sub> O <sub>4</sub> <sup>2-</sup> may be present
3.	Mixture + dil. H <sub>2</sub> SO <sub>4</sub> . Heat till the effervescences (if any) ceases. Add a pinch of MnO <sub>2</sub> (s)	Brisk effervescence (CO <sub>2</sub> ) is observed	C <sub>2</sub> O <sub>4</sub> <sup>2-</sup> confirmed
4. i.	CaCl <sub>2</sub> test: S.E. + CH <sub>3</sub> COOH (till acidic) + CaCl <sub>2</sub> solution	White ppt. soluble in dil. H <sub>2</sub> SO <sub>4</sub>	C <sub>2</sub> O <sub>4</sub> <sup>2-</sup> confirmed
ii.		Colour of KMnO <sub>4</sub> is discharged	C <sub>2</sub> O <sub>4</sub> <sup>2-</sup> confirmed

### 8.6.5.1 Chemical Reactions Involved

 Oxalate salts are decomposed by conc. H<sub>2</sub>SO<sub>4</sub> to give carbon monoxide (CO) and carbon dioxide (CQ<sub>2</sub>).

$$Na_2C_2O_4 + H_2SO_4 \xrightarrow{-\Delta} Na_2SO_4 + H_2O + CO\uparrow + CO_2\uparrow$$
 conc.

2. The gas evolved (CO) burns with a blue flame at the mouth of the test tube.

$$2\text{CO} + \text{O}_2 \xrightarrow{\Delta} 2\text{CO}_2$$

3. Addition of MnO<sub>2</sub> to mixture and dil. H<sub>2</sub>SO<sub>4</sub>, results in evolution of brisk effervescences (CO<sub>2</sub>).

$$Na_{2}C_{2}O_{4} + 2H_{2}SO_{4} + MnO_{2}$$

$$\longrightarrow Na_{2}SO_{4} + MnSO_{4} + 2H_{2}O + 2CO_{2}\uparrow$$

$$CaCl. test: Ovalates react with CaCl. solution 2.$$

**4.** CaCl<sub>2</sub> test: Oxalates react with CaCl<sub>2</sub> solution to give white ppt. of calcium oxalate (CaC<sub>2</sub>O<sub>4</sub>) which is soluble in dil. H<sub>2</sub>SO<sub>4</sub>.

$$\begin{aligned} \text{Na}_2 \text{C}_2 \text{O}_4 + \text{CaCl}_2 &\longrightarrow \text{CaC}_2 \text{O}_4 \downarrow + 2 \text{NaCl} \\ \text{CaC}_2 \text{O}_4 + \text{H}_2 \text{SO}_4 &\longrightarrow \text{CaSO}_4 + \text{H}_2 \text{C}_2 \text{O}_4 \\ & \text{dil.} \end{aligned}$$
 (Soluble)

**5.** To the above solution dil.  $H_2SO_4$  and  $KMnO_4$  solution are added. Colour of  $KMnO_4$  is discharged as oxalates reduce permanganate  $(MnO_4^{\Theta})$  to manganese(II)  $(Mn^{2+})$  ion.

$$5H_2C_2O_4 + 2 \text{ KMnO}_4 + 3H_2SO_4 \longrightarrow$$

$$KSO_4 + 2MnSO_4 + 8H_2SO_4 \longrightarrow$$

$$K_2SO_4 + 2MnSO_4 + 8H_2O + 10CO_2$$
Colourless

or 
$$[C_2O_4^{2-} \longrightarrow 2CO_2 + 2e^{\Theta}] \times 5$$

$$[MnO_4^{\Theta} + 8H^{\oplus} + 5e^{\Theta} \longrightarrow Mn^{2+} + 4H_2O] \times 2$$

$$5C_2O_4^{2-} + 2MnO_4^{\Theta} + 16H^{\oplus} \longrightarrow 10CO_2 + 2Mn^{2+} + 8H_2O$$

### ILLUSTRATION 8.3

- a. Arrange AgF, AgCl, AgBr and AgI in the increasing order of solubility in water.
- **b.** NO<sub>2</sub><sup>⊖</sup> interferes in the 'Ring Test' of NO<sub>3</sub><sup>⊖</sup>. Suggest a chemical method of removal of NO<sub>2</sub><sup>⊖</sup>.
- c. While testing oxalate, gas obtained burns with a blue flame initially but is put off instantly even as gas appears coming. Explain.
- **d.**  $I^{\odot}$  also interferes in the 'Ring Test' of  $NO_3^{\odot}$ . Suggest a chemical reagent that can remove  $I^{\odot}$ .
- e. Colourless solid (A) → (B) gas + (C) gas. Aqueous solutions of (A) and (B) turn blue litmus red while that of (C) turns red litmus blue. Aqueous solutions of (A) and (B) also give white ppt. with AgNO<sub>3</sub> solution soluble in aqueous solution of (C). Identify (A), (B) and (C).
- f. Can you detect Br<sup>⊖</sup> and I<sup>⊖</sup> by 'Layer Test' if present together?

### Sol.

- $a. \quad AgI < AgBr < AgCl < AgF$
- **b.** Boil the mixture with  $NH_4Cl$ ,  $NO_2^{\ominus}$  is decomposed as  $N_2$ :

$$NaNO_2 + NH_4Cl \xrightarrow{\Delta} NaCl + N_2 \uparrow + 2H_2O$$
**c.**  $H_2C_2O_4 \xrightarrow{\Delta} H_2O_{(l)} + CO_{(g)} + CO_{2(g)}$ 

- **d.**  $\operatorname{HgCl}_2$  removes  $\operatorname{I}^{\ominus}$  as  $\operatorname{HgI}_2$   $\operatorname{HgCl}_2 + 2\operatorname{I}^{\ominus} \longrightarrow \operatorname{HgI}_2 \downarrow + 2\operatorname{Cl}^{\ominus}$ Orange ppt
- e. (A): NH<sub>4</sub>Cl (B): HCl (C): NH<sub>3</sub>
- **f.** Reducing power  $I^{\Theta} > Br^{\Theta} > Cl^{\Theta} > F^{\Theta}$ . Add  $Cl_2$  water and  $CHCl_3$  into mixture of  $I^{\Theta}$  and  $Br^{\Theta}$

$$2I^{\ominus} + Cl_2 \xrightarrow{J} I_2 + 2Cl^{\ominus}$$
Violet
$$2Br^{\ominus} + Cl_2 \longrightarrow Br_2 + 2Cl^{\ominus}$$

$$2Br^{\Theta} + Cl_2 \longrightarrow Br_2 + 2Cl^{\Theta}$$
Orange yellow

Br<sub>2</sub> will also oxidise  $I^{\odot}$  to  $I_2$ . Thus, first there will be violet colour in CHCl<sub>3</sub> layer. Extract aq. layer (containing Br $^{\odot}$ ) and repeat adding Cl<sub>2</sub> water and CHCl<sub>3</sub>. Orange-yellow colour in CHCl<sub>3</sub> layer confirms Br $^{\odot}$ .

## 8.7 ANALYSIS OF THIRD CATEGORY ANIONS

### 8.7.1 TESTS FOR SULPHATE (SO<sub>4</sub><sup>2-</sup>) ION

		4		
S.No.	Experiment	Observation	Inference	
1. i. S.C.E. + dil. HCl (till acidic) + BaCl <sub>2</sub> solution		Curdy white ppt.	SO <sub>4</sub> <sup>2-</sup> may be present	
ii.	White ppt (1) + conc. HCl or conc. HNO <sub>3</sub>	The ppt. does not dissolve	SO <sub>4</sub> <sup>2-</sup> confirmed	
2.	S.C.E. + CH <sub>3</sub> COOH (till acidic) + lead acetate solution	White ppt.	SO <sub>4</sub> <sup>2-</sup> confirmed	

### Chemical Reactions Involved $\frac{7^{1/3}}{1}$ $\frac{Na_2SO_4 + BaCl_2}{1}$ $\longrightarrow BaSO_4 \downarrow + 2NaCl_4$ $BaSO_4$ + conc. HCl $\longrightarrow$ ppt. does not dissolve $_{1. \text{Na}_2\text{SO}_4} + (\text{CH}_3\text{COO})_2\text{Pb} \longrightarrow \text{PbSO}_4 \downarrow + 2\text{CH}_3\text{COONa}$

### 1.2 TESTS FOR BORATE (BO<sub>3</sub> 1-) ION

No.	Experiment	Observation	Inference
1.	In a boiling tube, fitted with cork and glass tube take mixture. Add 1 mL conc. H <sub>2</sub> SO <sub>4</sub> and 4–5 mL of ethyl or methyl alcohol warm and burn the ensuing gas in the flame.	(C <sub>2</sub> H <sub>5</sub> O) <sub>3</sub> B burn with green edged	BO <sub>3</sub> <sup>3-</sup> confirmed
2.	Mixture + powdered CaF <sub>2</sub> + little of conc H <sub>2</sub> SO <sub>4</sub> to make a paste. Bring this paste, on the end of glass rod, near the edge of flame without touching it.		BO <sub>3</sub> <sup>3-</sup> confirmed

### 8.7.2.1 Chemical Reactions Involved

1. 
$$2\text{Na}_2\text{BO}_3 + 3\text{H}_2\text{SO}_4 \longrightarrow 2\text{H}_3\text{BO}_3 + 3\text{Na}_2\text{SO}_4$$

$$\begin{aligned} \text{H}_3\text{BO}_3 + 3\text{C}_2\text{H}_5\text{OH} & \xrightarrow{\Delta} (\text{C}_2\text{H}_5\text{O})_3\text{B} \uparrow + 3\text{H}_2\text{O} \\ \text{Burns with green edged} \\ \text{flame (volatile)} \\ \text{(triethoxyborate)} \end{aligned}$$

This test is performed in test tube and not in china dish, as Cu and Ba both respond to this test. In this way, only vapours of triethoxyborte are able to reach the mouth of the test tube and gives green edged flame, whereas Cu and Ba are left behind.

2. 
$$H_3BO_3 \longrightarrow B_2O_3 + H_2O$$
 $CaF_2 + H_2SO_4 \longrightarrow CaSO_4 + 2HF$ 
 $B_2O_3 + 6HF \longrightarrow 2BF_3 \uparrow + 3H_2O$ 
Burns with green flame (volatile)

This test is quite reliable, as Cu and Ba do not interfere.

## 8.7.3 TESTS FOR PHOSPHATE (PO<sub>4</sub><sup>3-</sup>) ION

	123131313		
S.No.	Experiment	Observation	Inference PO <sub>4</sub> <sup>3-</sup>
1.	Mixture + conc. HNO <sub>3</sub> .Boil and cool. Add ammonium molybdate solution in excess, boil and	Canary yellow ppt. Insoluble in NH <sub>4</sub> OH/NaOH	confirmed

2.	S.E. + dil. HCl till acidic (~1N HCl) + Zirconyl nitrate reagent	White geletinious ppt. of zirconyl phosphate	PO <sub>4</sub> <sup>3-</sup> confirmed
3.	S.E. + Magnesium nitrate reagent	Crystalline white ppt.	PO <sub>4</sub> <sup>3-</sup> confirmed

#### 8.7.3.1 Chemical Reactions Involved

- 1.  $Na_3PO_4 + 12 (NH_4)_2MoO_4 + 24 HNO_3 \xrightarrow{\Delta}$  $(NH_4)_3PO_4 \cdot 12MoO_3 \downarrow + 21 NH_4NO_3 + 3NaNO_3 + 12H_2O_3 + 12$ Canary yellow ppt.
  - i. Arsenates give a similar test on boiling. If As is present then test for PO<sub>4</sub><sup>3-</sup> with filtrate of group II.
  - ii. Reducing agents such as S<sup>2-</sup>, SO<sub>3</sub><sup>2-</sup> affect the reaction as they produce 'molybdenum blue' (MoO<sub>2</sub>·xH<sub>2</sub>O). The solution therefore turns blue and should be destroyed before carrying out this test and hence the mixture is first boiled with conc. HNO3, an oxidising agent.

2. 
$$Na_3PO_4 + HCl \longrightarrow Na_2HPO_4 + NaCl$$
  
 $2Na_2HPO_4 + 2 HCl + ZrO (NO_3)_2$   
 $\longrightarrow ZrO(H_2PO_4)_2 \downarrow + 2NaCl + 2NaNO_3$   
White geletinous ppt.

3. 
$$Na_2HPO_4 + Mg(NO_3)_2 + NH_3 \longrightarrow Mg(NH_4)PO_4 \downarrow + 2NaNO_3$$
  
Crystalline white ppt.

Magnesium nitrate reagent is a solution containing magnesium nitrate Mg(NO<sub>3</sub>)<sub>2</sub>, ammonium nitrate (NH<sub>4</sub>NO<sub>3</sub>) and a little aqueous NH<sub>3</sub>.

On treatement with magnesium nitrate reagent white crystalline ppt. of Mg(NH<sub>4</sub>)PO<sub>4</sub>·6H<sub>2</sub>O (magnesium ammonium phosphate) is produced.

### TOT THEODISE (FO) ION

S.No.	Experiment	Observation	Inference	
1. i. Mixture + conc. H <sub>2</sub> SO <sub>4</sub> . Heat.		Colourless gas (HF) is evolved which fumes in moisture and test tube acquires a greasy appearance	F <sup>⊕</sup> may be present	
ii.	In above solution add sand. Heat. Bring a glass rod moistened with water near the mouth of the test tube	White waxy deposit (H <sub>4</sub> SiO <sub>4</sub> ) on the moist part of glass rod	F <sup>⊖</sup> confirmed	
2. i.	S.E. + CH <sub>3</sub> COOH (till acidic) + CaCl <sub>2</sub> solution	White ppt. insoluble in dil. H <sub>2</sub> SO <sub>4</sub>	F <sup>⊖</sup> confirmed	
ii.	Above ppt. + dil. H <sub>2</sub> SO <sub>4</sub> + few drops of KMnO <sub>4</sub> solution	The colour of KMnO <sub>4</sub> is not discharged	F <sup>©</sup> confirmed	

### 8.7.4.1 Chemical Reactions Involved

1. a. NaF + 
$$H_2SO_4 \xrightarrow{\Delta} NaHSO_4 + HF \uparrow$$

**b.** 
$$4HF + SiO_2 \xrightarrow{\Delta} SiF_4 + 2H_2O$$
  
 $3SiF_4 + 4H_2O \xrightarrow{} 2H_2[SiF_6] + H_4SiO_4 \downarrow$   
White (silicis acid)

HF gas being corrosive, attacks silica present in the glass test tube to produce oily drops. The corrosive action of HF is also responsible for the greasy appearance.

Fluorosilicic acid [H<sub>2</sub>(SiF<sub>6</sub>)], which is known only in aqueous solution, is decomposed into silicon tetrafluoride and hydrofluoric acid on evaporating the aqueous solution.

$$H_2SiF_6 \longrightarrow SiF_4 \uparrow + 2HF \uparrow$$
2.  $2NaF + CaCl_2 \longrightarrow CaF_2 \downarrow + 2NaCl$ 
White ppt.

CaF<sub>2</sub> is insoluble in dil. H<sub>2</sub>SO<sub>4</sub> and does not react with KMnO<sub>4</sub> and hence colour of KMnO<sub>4</sub> is not discharged.

# 8.8 SPECIFIC TESTS FOR COMBINATIONS OF ACID RADICALS

Many times, while performing the test for the presence of a particular anion in the given mixture, the presence of some other anions may cause interference in the usual tests for the radical. In such cases special tests are performed or usual tests are modified in order to detect such radicals simultaneously and conveniently. Some such cases are discussed below.

### 8.8.1 CARBONATE $(CO_3^{2-})$ AND SULPHITE $(SO_3^{2-})$

Carbonates and sulphites decompose on treatment with dil.  $H_2SO_4$  to give  $CO_2$  and  $SO_2$  gases respectively, both of which turn lime water milky. The dichromate test for  $SO_3^{2-}$  however is not influenced by  $CO_3^{2-}$ . Hence  $SO_3^{2-}$  interfere with the test for  $CO_3^{2-}$  but  $CO_3^{2-}$  does not interfere with the test for sulphite. To test for the presence of carbonate and sulphite in a mixture the following test is performed:

g performed.				
Experiment		Observation	Inference	
Take the mixture and small amount of powdered K <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub> in a test tube. Add a little of dil. H <sub>2</sub> SO <sub>4</sub> and warm. Pass the gas evolved through lime water	i. ii.	If the contents of test tube becomes green and lime water turns milky If the contents of test tube remains unchanged and lime water turns milky	SO <sub>3</sub> <sup>2-</sup> as well as CO <sub>3</sub> <sup>2-</sup> are present  Only CO <sub>3</sub> <sup>2-</sup> is present	
	iii.	If the contents of test tube becomes green and lime water remains unchanged	Only SO <sub>3</sub> <sup>2-</sup> is present.	

$$\begin{aligned} \text{Na}_2\text{CO}_3 + \text{H}_2\text{SO}_4 &\longrightarrow \text{Na}_2\text{SO}_4 + \text{CO}_2 \uparrow + \text{H}_2\text{O} \\ \text{dil.} & \text{CO}_2 + \text{Ca}(\text{OH})_2 &\longrightarrow \text{CaCO}_3 \downarrow + \text{H}_2\text{O} \\ \text{Lime water} & \text{Milky} & \text{Hilky} & \text{CaCO}_3 + \text{H}_2\text{O} + \text{CO}_2 &\longrightarrow \text{Ca}(\text{HCO}_3)_2 \\ \text{Excess} & \text{Colourless} & \text{Colourless} & \text{Na}_2\text{SO}_3 + \text{H}_2\text{O} + \text{SO}_2 \uparrow \\ \text{dil.} & \text{SO}_2 + \text{Ca}(\text{OH})_2 &\longrightarrow \text{CaSO}_3 + \text{H}_2\text{O} \\ & \text{Milky} & \text{CaCO}_3 + \text{SO}_2 &\longrightarrow \text{Ca}(\text{HCO}_3)_2 \\ & \text{Colourless} &$$

In presence of  $K_2Cr_2O_7$ ,  $SO_3^{\ 2-}$  ions which produce  $SO_2$  reacts with  $K_2Cr_2O_7$  to give green coloured compound, whereas  $CO_2$  does not react with  $K_2Cr_2O_7$ .

$$K_2Cr_2O_7 + H_2SO_4 + 3SO_2 \longrightarrow K_2SO_4 + Cr_2(SO_4)_3 + H_2O_4$$

### 8.8.2 CARBONATE ( $CO_3^{2-}$ ) AND OXALATE ( $C_2O_4^{2-}$ )

Carbonates are decomposed by both dil. and conc.  $H_2SO_4$ , whereas oxalates are decomposed by conc.  $H_2SO_4$  only to give  $CO_2$ . Carbonate interferes in this test for oxalates. However  $CO_3^{2-}$  does not interfere with  $CaCl_2$  for  $C_2O_4^{2-}$ .

 $CO_3^{2-} \longrightarrow Lime water test.$ 

 $C_2O_4^{2-} \longrightarrow CaCl_2$  test. (Already discussed in tests for oxalate ion) An alternate method may be employed to test for carbonate and oxalate in a mixture:

S.No.	Experiment	Observation	Inference
1.	Heat the mixture with dil. H <sub>2</sub> SO <sub>4</sub> and pass the gas through lime water	Lime-water turns milky	CO <sub>3</sub> <sup>2-</sup> present
2.	Heat till effervescence ceases. Add a pinch of MnO <sub>2</sub> solid	Fresh effervescence is observed	C <sub>2</sub> O <sub>4</sub> <sup>2-</sup> present

a. 
$$Na_2CO_3 + H_2SO_4 \longrightarrow Na_2SO_4 + CO_2 \uparrow + H_2O$$
dil.
$$CO_2 + Ca(OH)_2 \longrightarrow CaCO_3 \downarrow + H_2O$$
Lime water Milky

**b.** 
$$Na_2C_2O_4 + H_2SO_4 + MnO_2 \longrightarrow Na_2SO_4 + MnSO_4 + 2H_2O + 2CO_2$$

8.8.3 NITRITE ( $NO_2^{\odot}$ ) AND NITRATE ( $NO_3^{\odot}$ )

 $NO_2^{\ominus}$  can be detected in presence of  $NO_3^{\ominus}$  by treatment with dil.  $H_2SO_4$ , KI-starch test or by ring test or  $\alpha$ -naphthyl amine, sulphanilic acid test. However  $NO_3^{\ominus}$  cannot be detected in the presence of  $NO_2^{\ominus}$ , because it gives all the test of  $NO_2^{\ominus}$ .  $NO_2^{\ominus}$  and  $NO_3^{\ominus}$  in a mixture can be detected as follows:

Nitrite is completely decomposed by one of the following methods: **a.** Boiling W.E./S.E. with solid NH<sub>4</sub>Cl added in pinches till

effervescence ceases.

$$NH_4NO_2 + NH_4Cl \longrightarrow NH_4NO_2 + NaCl$$

$$NH_4NO_2 \longrightarrow N_2 \uparrow + 2H_2O$$

Boiling with dil. H<sub>2</sub>SO<sub>4</sub> and solid urea in pinches till effervescence ceases.

Adding little sulphanilic acid to a solution or S.E. The last named is most efficient.  $NO_3^{\ominus}$  is now tested using this solution by using ring test or converting  $NO_3^{\ominus}$  to  $NO_2^{\ominus}$  by adding Zn dust and dil.  $H_2SO_4$  and testing for  $NO_2^{\ominus}$  ion.

## $_{\S,8,4}$ NITRATE (NO $_3^{\odot}$ ), BROMIDE (Br $^{\odot}$ ) AND IODIDE (I $^{\odot}$ )

All are decomposed by conc.  $H_2SO_4$  to give  $NO_2$ ,  $Br_2$ ,  $I_2$  and  $I_2$  are brown,  $I_2$  is violet in colour. The brown ring test for  $NO_3^{\odot}$  cannot be applied effectively because  $Br_2$  and  $I_2$  evolved obscure the brown ring due to  $NO_3^{\odot}$ . Therefore they are detected in the mixture as follows:

- a. Br<sup>©</sup> and I<sup>©</sup> can be detected by layer test, NO<sub>3</sub><sup>©</sup> does not interfere. Nitrate is converted to NO<sub>2</sub><sup>©</sup> by treatment with Zn metal and conc. H<sub>2</sub>SO<sub>4</sub>, and then NO<sub>2</sub><sup>©</sup> is detected by usual test. If I<sup>©</sup> is present, the colour of the solution will turn blue violet on adding starch solution without adding KI solution.
- b. Remove halides by adding a saturated solution of ammoniacal silver sulphate solution  $[Ag(NH_3)_2]_2SO_4$  (prepared by dissolving 7.8 g of pure silver sulphate in 25 mL of 4N NH<sub>4</sub>OH and diluting to 100 mL with water). A precipitate of AgBr or AgI will be formed. Filter the precipitate and test for  $NO_3^{\ominus}$  in the filterate.

## 8.8.5 CHLORIDE ( $Cl^{\odot}$ ), BROMIDE ( $Br^{\odot}$ ) AND lodide ( $I^{\odot}$ )

Chlorides, bromides and iodides are all decomposed by conc.  $\rm H_2SO_4$  producing HCl, HBr + Br\_2 and  $\rm I_2$  respectively. When any two or all the three are present in the mixture, the characterisation of evolved gases is not possible because their colours and smells may be intermixing. All these anions give precipitate with AgNO\_3 in solution. Hence this test also will not give characteristic and distinctive result. Following tests can be carried out to detect all the three in the mixture.

- The presence of Cl<sup>Θ</sup> can be confirmed by chromylchloride test (Br<sup>Θ</sup> and I<sup>Θ</sup> do not give similar tests). Br<sup>Θ</sup> and I<sup>Θ</sup> are detected by layer test (Cl<sup>Θ</sup> does not interfere).
- 2. Layer test for Br<sup>©</sup> and I<sup>©</sup>: S.C.E. + CCl<sub>4</sub>/CS<sub>2</sub>/CHCl<sub>3</sub> + Cl<sub>2</sub> water. Shake the contents vigorously. Following changes may take place.
  - a. Organic layer remains colourless: Both Br<sup>©</sup> and I<sup>©</sup> are absent.
  - b. Organic layer turns violet, this shows the presence of I<sup>□</sup>. Add excess of Cl<sub>2</sub> water. Organic layer becomes colourless. Only I<sup>□</sup> is present.
  - c. If organic layer first turns violet, then brown on excess addition of  $\operatorname{Cl}_2$  water. Both  $\operatorname{I}^{\ominus}$  and  $\operatorname{Br}^{\ominus}$  are present.

**d.** If organic layer turns brown in colour. Only  $Br^{\Theta}$  is present. This test is based on the easier replacement of  $I^{\Theta}$  from a salt than that of  $Br^{\Theta}$  from its salt by chlorine.

$$Cl_2 + 2I^{\bigcirc} \longrightarrow 2CI^{\bigcirc} + I_2$$
 (first)

$$Cl_2 + 2Br^{\Theta} \longrightarrow 2Cl^{\Theta} + Br_2$$
 (later

Reduction potential of  $F_2 > CI_2 > Br_2 > I_2$ . Hence  $CI_2$  can oxidise  $I^{\Theta}$  to  $I_2$  faster than  $Br^{\Theta}$  to  $Br_2$ .

### 8.8.6 NITRATE (NO<sub>3</sub><sup>©</sup>) AND BROMIDE (Br<sup>©</sup>)

Nitrates and bromides are decomposed by conc. H<sub>2</sub>SO<sub>4</sub> producing NO<sub>2</sub> and Br<sub>2</sub> gases respectively, both of which are brownish in colour and turn KI-starch paper blue in colour. These are detected in a mixture as follows.

 $\mathrm{Br}^{\Theta}$  can be tested by layer test or  $\mathrm{AgNO_3}$  test ( $\mathrm{NO_3}^{\Theta}$  does not interfere).  $\mathrm{NO_3}^{\Theta}$  is detected by converting it into  $\mathrm{NO_2}^{\Theta}$  by adding a zinc dust and small amount of dil.  $\mathrm{H_2SO_4}$  to a portion of S.E. and boiling for some time and perform the test for  $\mathrm{NO_2}^{\Theta}$  ion.

### 8.8.7 NITRATE (NO<sub>3</sub><sup>☉</sup>) AND IODIDE (I<sup>☉</sup>)

The conc.  $H_2SO_4$  test is not disinctive for these two anions when present together in a mixture because they evolve  $NO_2$  and  $I_2$  gases which are brown and violet respectively. These anions can be detected and confirmed by the following test:

 $\begin{array}{c} \text{I}^{\circleddash} -\text{layer test or AgNO}_3 \text{ test} \\ \text{NO}_3^{\circleddash} -\text{Convert to NO}_2^{\circleddash} \text{ by adding dil. H}_2\text{SO}_4 \\ &+\text{Zn dust and then apply tests for NO}_2^{\circleddash} \end{array}$ 

### 8.8.8 FLUORIDE (F $^{\odot}$ ) AND OXALATE (C<sub>2</sub>O<sub>4</sub> $^{2-}$ )

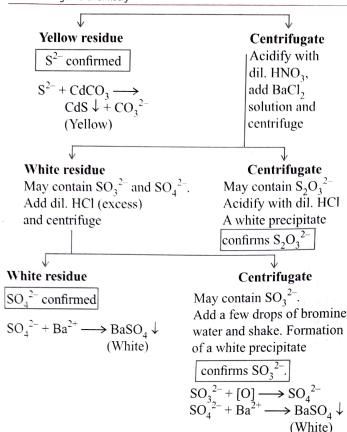
Fluoride and oxalate are rarely given simultaneously in the mixture. They give white ppt. of CaF<sub>2</sub> and CaC<sub>2</sub>O<sub>4</sub> when CaCl<sub>2</sub> solution is added to their acidic solution (S.C.E. acidified with CH<sub>3</sub>COOH). These precipitates are distinguished as follows.

Treat the ppt. with dil. H<sub>2</sub>SO<sub>4</sub>. CaC<sub>2</sub>O<sub>4</sub> dissolves whereas CaF<sub>2</sub> is insoluble.

	S.E. + dil. CH <sub>3</sub> COOH (till acidic) + CaCl <sub>2</sub> solution	White ppt. (CaF <sub>2</sub> /CaC <sub>2</sub> O <sub>4</sub> )	
2.	Dissolve the ppt. in dil. $H_2SO_4$	Filterate (CaC <sub>2</sub> O <sub>4</sub> ) Residue (CaF <sub>2</sub> )	
3.	Filterate + dil. KMnO <sub>4</sub>	Colour of KMnO <sub>4</sub> is discharged	C <sub>2</sub> O <sub>4</sub> <sup>2-</sup> confirmed
4.	Residue + dil. H <sub>2</sub> SO <sub>4</sub> + KMnO <sub>4</sub> solution	Colour of KMnO <sub>4</sub> is not discharged	F <sup>⊖</sup> confirmed

# 8.8.9 Sulphide (S $^{2-}$ ), Sulphite (S $O_3^{\ 2-}$ ), Thiosulphate (S $_2O_3^{\ 2-}$ ) and Sulphate (S $O_4^{\ 2-}$ )

Take 10 drops S.C.E. and shake it in 10 mg of CdCO<sub>3</sub>. Heat for 1 min and centrifuge.



### 8.8.10 Phosphate ( $PO_4^{3-}$ ) and Arsenate ( $AsO_4^{3-}$ )

The salts of arsenic are converted to arsenates when boiled with conc. HNO<sub>3</sub>. Thus when a mixture containing arsenic and phosphate is tested for the presence of PO<sub>4</sub> <sup>3-</sup> by adding conc. HNO<sub>3</sub> and ammonium molybdate solution, arsenic is also precipitated as ammonium arsenate along with ammonium phosphomolybdate; both of which are yellow in colour. However zirconyl nitrate test for PO<sub>4</sub> <sup>3-</sup> is not influenced by As<sup>3+</sup>. When As<sup>3+</sup> is present in a mixture containing PO<sub>4</sub> <sup>3-</sup>, PO<sub>4</sub> <sup>3-</sup> is tested in the filterate of group II after removal of As<sup>3+</sup> as As<sub>2</sub>S<sub>3</sub>.

### ILLUSTRATION 8.4

- **a.** (A) + KBr  $\longrightarrow$  yellow ppt. (B)
  - (A) + conc.  $H_2SO_4 \xrightarrow{\Delta}$  brown vapours intensified with Cu-turnings.
  - (B) dissolves in hypo forming a soluble complex (C). What are (A), (B) and (C) and explain their reactions?
- **b.**  $SO_3^{2-}$  and  $SO_4^{2-}$  both give white ppt. with  $BaCl_2$  solution. How is  $SO_3^{2-}$  detected in presence of  $SO_4^{2-}$ ?
- c. Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub>·10H<sub>2</sub>O + conc. H<sub>2</sub>SO<sub>4</sub> $\xrightarrow{\Delta}$ (A)  $\xrightarrow{CH_3OH, \Delta}$  (B). Identify (A) and (B).
- **d.** (A) + dil.  $H_2SO_4 \xrightarrow{\Delta} gas$  (B).

Gas (B) turns  $K_2Cr_2O_7/H^{\oplus}$  solution green. Aq. solution of (A) + BaCl<sub>2</sub>  $\longrightarrow$  white ppt. (C).

Filtrate after removing (C) +  $Br_2$  water  $\longrightarrow$  white ppt. (C). Identify (A), (B) and (C).

e.  $SO_4^{2-}$  also gives white ppt. with lead acetate but ppt. dissolves in ammonium acetate solution. Explain.

#### Sol.

- **a.** (A):  $AgNO_3$  (B): AgBr (C):  $Na_3[Ag(S_2O_3)_2]$
- b. BaSO<sub>4</sub> is insoluble in conc. HCl, while BaSO<sub>3</sub> remains soluble. Separate BaSO<sub>4</sub> and add Br<sub>2</sub> water into filtrate. SO<sub>3</sub><sup>2-</sup> is oxidised to SO<sub>4</sub><sup>2-</sup> and gives white ppt. of BaSO<sub>4</sub>.

$$Br_2 + H_2O \longrightarrow 2HBr + O$$
  
 $BaSO_3 + O \longrightarrow BaSO_4 \downarrow$ 

- **c.** (A):  $H_3BO_3$ 
  - (B): (CH<sub>3</sub>O)<sub>3</sub>B, burns with green edged flame.
- **d.** (A):  $SO_3^{2-} + SO_4^{2-}$  (B):  $SO_2$  (C):  $BaSO_4$
- e.  $2CH_3COONH_4 + PbSO_4 \longrightarrow$ White ppt.  $(CH_3COO)_2Pb + (NH_4)_2SO_4$ Soluble

## 8.9 IDENTIFICATION OF BASIC RADICALS (CATIONS)

The identification of basic radicals is carried out by performing the following types of tests:

- 1. Preliminary dry tests
- 2. Systematic examination in solution i.e., wet tests.

### 8.9.1 PRELIMINARY DRY TEST

These tests can give very useful informtion about the cations and anions present in a mixture. Since these tests are neither systematic nor much reliable, not much time should be spent on performing these tests.

### **8.9.2 COLOUR**

Observe colour of the given mixture and draw the conclusion from Table 8.2.

Table 8.2 Colour of the mixture

Colour	Inference	Colour	Inference
Blue	Cupric salts	Yellow or brown	Ferric salts
Green or blue	Hydrated copper salts	Pale pink	Manganese salts
Deep-blue	Anhydrous cobalt salts	Rose-red	Cobalt salts, HgI <sub>2</sub>
Green	Hydrated nickel salts	Dark- green or purple	Chromic salts
Light green	Ferrous salts	Colourless	Salts of K, NH <sub>4</sub> <sup>⊕</sup> , Pb, Cd, As, Al, Na, Ca, Ba, Sr

If the salt is colourless; Cu, Fe, Cr, Co, Ni, Mn salts are probably absent.

Anhydrous copper sulphate is a white solid.

In a mixture of salts, the dark colour may mask a light colour of the colour may be altogether different.

In a mixture of coloured salt with a white salt, the absence of presence of the latter cannot be predicted.

### 9,3 SMELL OF THE SALT OR MIXTURE

ace a pinch of the salt on a watch glass. Moisten it with water then rub it with your thumb and finger, smell and draw the terence.

### ble 8.3 Smell of the mixture

No.	Observation	Inference	
1.	Smell of NH <sub>3</sub> gas	Ammonium radical, NH₄ <sup>⊕</sup>	
2.	Smell of rotten eggs	Sulphide (S <sup>2-</sup> )	

lote: The absence of any smell does not mean the absence of the radical.

### 9.4 DENSITY

the mixture on a piece of paper and then place it on your palm.

### ble 8.4 Density of the mixture

No.	Smell	Inference	
1.	Heavy	Pb or Ba salts	
2.	Light or fluffy powder	Carbonates of Zn, Mg, Al	
3.	Neither light nor heavy	Pb, Ba, Al, Mg and Ca salts may be absent	

### .9.5 Dry-heating Test

rongly by keeping it almost horizontal over the flame. Observe changes and infer from the Table 8.5.

Inference

### able 8.5 Dry-heating test

**Observations** 

No.

	11110101100	
The solid melts	Hydrated salts	
The solid swells	Borate, phosphate or alums	
Crackling sound on heating	Pb(NO <sub>3</sub> ) <sub>2</sub> , Ba(NO <sub>3</sub> ) <sub>2</sub> , KBr	
A sublimate forms		
White	NH₄ <sup>⊕</sup> , As salts	
Grey or black	Hg salt	
Purple or black solid	Iodide	
Change in colour of the salts		
Yellow when hot and white when cold	Zn salt	

ii.	Blue when hot and rosy red when cold	Hydrated Co salt	
iii.	White when hot and blue when cold	CuSO <sub>4</sub> ·5H <sub>2</sub> O	
iv.	Dark-brown when hot and yellow when cold	Pb salt	
v.	Dirty white or yellow when hot and green when cold	Ni, Fe (II) salts	
vi.	Black residue	The metal whose oxide is black, Cu Fe, Co, Ni	
vii.	Salt glows on heating	Ca, Mg, Al salts	
6.	Evolution of a coloured gas		
i.	Brown gas	Nitrates of heavy metals or bromides	
ii.	Violet vapour	Iodides	
7.	Water drops in the upper portion of test tubes.	Hydrated salts	

### 8.9.6 FLAME TEST

Certain volatile substances (especially metal chlorides) when heated in a bunsen flame impart a characteristic colour to the flame by means of which the substance can be identified. Colour of the flame is different when it is viewed through a blue or double blue glass.

#### **Procedure:**

- 1. Put some conc. HCl in a china dish. Immerse the loop of the platinum wire in conc. HCl and heat it on the non-luminous flame. If it imparts any colour to the flame, repeat the process of immersing it in conc. HCl and then heating it in a flame until the colour is no longer visible.
- 2. Wash the watch glass or china dish and now place a little of the mixture and then moisten it with conc. HCl so that the metal chloride may be produced.
- 3. Take a little of the moistened mass on the loop of a platinum wire and heat it in a bunsen flame.
- 4. Observe the colour of the flame.
  - a. With naked eye
  - **b.** Through a blue glass

### Table 8.6 Flame test for cations

Flame colour with naked eye	Flame colour through blue glass	Inference
Dark-green	Bluish-green	Cu <sup>2+</sup>
Pink-violet	Pink	Cu K <sup>⊕</sup>
Brick-red	Light-green	Ca <sup>2+</sup>
Grassy-green	Bluish-green	Ba <sup>2+</sup>
Crimson (deep-red)	Purple	Sr <sup>2+</sup>

#### 8.9.7 BORAX BEAD TEST

- 1. Heat the loop of the platinum wire in a flame of the bunsen burner. Then dip the hot loop into powdered borax and again heat it to form a clear, transparent and glassy bead. If the bead obtained is not clear and transparent jerk it off and perform again.
- **2.** Just touch the hot bead with the mixture so that only a few particles stick to it.
- **3.** Then heat it in the oxidising flame and observe colour of the bead when hot. Cool it and again observe its colour when cold.
- **4.** Heat it again but now in the reducing flame and observe its colour when hot. Cool it and again observe its colour when cold.

#### Table 8.7 Borax bead test

Colour of the bead in oxidising flame When hot		delegat of the beda in		Inference		
		When cold	When hot	When cold		
1.	Brown	Yellow	Bottle green	Yellow green	Fe	
2.	Green	Blue	Colourless	Red	Cu	
3.	Brown	Brown	Grey or black	Grey or black	Ni	
4.	Pale-purple	Pale-purple	Colourless	Colour- less	Mn	
5.	Green	Green	Green	Green	Cr	
6. Blue		Blue	Blue	Blue	Co	

## 8.9.7.1 Chemistry of Borax Bead Test

When powdered borax is heated strongly in a bunsen flame, it loses its water of crystallisation and forms colourless transparent glass like bead which is made up of sodium metaborate and boric anhydride.

$$Na_2B_4O_7 \cdot 10H_2O + H_2O \longrightarrow \underbrace{2NaBO_2 + B_2O_3}_{Transparent bead} + 10H_2O$$

Boric anhydride reacts with certain metal salts to form coloured metaborates.

#### 8.9.7.2 In Oxidising Flame

3. 
$$B_2O_2 + CoSO_4 \longrightarrow Co(BO_2)_2 + SO_3$$
Cobalt
Cobalt
Sulphate
metaborate

4. 
$$B_2O_3 + Fe_2O_3 \longrightarrow 2Fe(BO_2)_3$$
Ferric Ferric
oxide metaborate

#### 8.9.7.3 In Reducing Flame

Certain metaborates are reduced to the free metal in a reducing flame. For metals with variable valence, the metaborate changes to lower valence state.

1. 
$$2Cu(BO_2)_2 + C \longrightarrow 2CuBO_2 + B_2O_3 + CO$$
  
 $2CuBO_2 + C \longrightarrow 2Cu + B_2O_3 + CO$ 

2. 
$$Ni(BO_2)_2 + C \longrightarrow Ni + B_2O_3 + CO$$

3. 
$$2\text{Fe}(BO_2)_3 + C \longrightarrow 2\text{Fe}(BO_2)_2 + B_2O_3 + CO$$

## 8.9.7.4 Notes for Borax Bead Test

- 1. Only coloured salts give borax bead test. Do not perform this test if the salt is colourless.
- 2. The bead should be clear, transparent and glass like. If it is not so, jerk it off from the loop and start afresh.
- 3. While heating, the loop of the platinum wire should be kept vertical.
- **4.** Only a few particles of the mixture should be taken for the borax bead test.
- 5. Observe the colour of bead, when hot as well as when cold.

#### 8.9.8 CHARCOAL CAVITY TEST

#### **Procedure:**

- 1. Bore a fresh cavity in a clean charcoal block with the help of a knife or cavity borer.
- Mix about (5-10 mg) of powdered salt with about (40-50 mg) of anhydrous sodium carbonate or fusion mixture (mixture of equal amounts of Na<sub>2</sub>CO<sub>3</sub> and K<sub>2</sub>CO<sub>3</sub>).
- **3.** Place small amount of the salt into a freshly bored cavity, press it with 1–2 drops of water.
- 4. Put this mixture to flame by means of a blow pipe for 2-5 min.
- 5. Observe the colour of bead, the colour of residue and the colour of incrustation formed if any when hot as well as when cold.

## Table 8.8 Charcoal cavity test

Colour of residue or incrustation			Colour of bead	Inference
When hot		n hot When cold		
1.	Yellow	White	None	Zn
2.	Dark-red brown	Yellow	Soft white marks paper	Pb
3.	Chocolate brown	Chocolate brown	None	Cd
4.	Red flakes	Red flakes	Red flakes	Cu
5.	White	White (gar- lic odour)	None	As

6. None	None	Slightly white does not mark paper	Ag
7. Black	Black	None	Fe, Co, Ni,
8. White	White None	None	Mn
		2. Offe	Ca, Ba, Sr, Al, Mg

perform the test with a newly-bored cavity.

. The cavity should not be deep.

1 The mixture should be moistened with a drop of water. Otherwise, there are every chances of it being blown away.

4. The mixture should be completely covered with flame while heating.

5. Any deflagration of the mixture on heating indicates the presence of nitrate.

# 89.8.1 Chemistry of Charcoal Cavity Test

Heating of the given salt with solid sodium carbonate or fusion salt ioms the corresponding carbonates of the basic radicals.

$$PbCl_{2(s)} + Na_2CO_{3(s)} \longrightarrow PbCO_{3(s)} + 2NaCl_{(s)}$$
  
Lead chloride Sod, carbonate

Lead chloride Sod. carbonate Lead carbonate

$$CuSO_{4(s)} + Na_2CO_{3(s)} \longrightarrow CuCO_{3(s)} + Na_2SO_{4(s)}$$

Copper sulphate Sod. carbonate Copper carbonate

1. Metal carbonates decompose into metal oxides. The metal oxides, if volatile, form incrustation (crust) around the cavity.

$$CdCO_{3(s)} \longrightarrow CdO_{(s)} + CO_{2(g)}$$

Cadium carbonate Cadium oxide

$$CuCO_{3(s)} \longrightarrow CuO_{(s)} + CO_{2(g)}$$

Copper carbonate Cupric oxide

$$ZnCO_{3(s)} \longrightarrow ZnO_{(s)} + CO_{2(g)}$$

Zinc carbonate Zinc oxide

2. The unstable metallic oxides further decompose into free metals to form metallic beads or scales.

$$Pb(NO_3)_{2(s)} + Na_2CO_{3(s)} \longrightarrow PbCO_{3(s)} + NaNO_{3(s)}$$

Sod. carbonate

Lead carbonate Sod. nitrate

$$PbCO_{3(s)} \longrightarrow PbO_{(s)} + CO_{2(g)}$$

Lead carbonate Lead oxide (yellow)

$$PbO_{(s)} + C_{(s)} \longrightarrow Pb_{(s)} + CO_{(g)}$$

Lead oxide Carbon Metallic bead

$$CuCO_{3(s)} \longrightarrow CuO_{(s)} + CO_{2(g)}$$

Cupric carbonate Cupric oxide

$$CuO_{(s)} + C_{(s)} \longrightarrow Cu_{(s)} + CO_{(g)}$$

Copper (red) Cupric oxide carbon

# 8.9.9 COBALT NITRATE TEST OR RINMANN'S TEST

#### **Procedure:**

- 1. Bore a fresh cavity in a charcoal block.
- 2. Place the given salt alone in this cavity and heat it for 10-15 sec with flame using blow-pipe.
- 3. Cool it, add 1-2 drops of cobalt nitrate solution and then heat it with the tip of the flame (oxidising) using blow pipe.
- 4. Observe the colour of the residue.

#### Table 8.9 Cobalt nitrate test

Colour of residue		olour of residue Inference	
1.	Green residue	Zn	CoO·ZnO
2.	Pink residue	Mg	CoO·MgO
3.	Blue residue	Al when PO <sub>4</sub> <sup>3-</sup> and BO <sub>3</sub> <sup>3-</sup> are absent	CoO·Al <sub>2</sub> O <sub>3</sub>
4.	Blue residue	PO <sub>4</sub> <sup>3-</sup> in absence of Al	NaCo.PO <sub>4</sub>

#### Note:

- 1. Cobalt nitrate test is performed only when residue left in the charcoal cavity test is white.
- 2. Only zinc, magnesium and aluminium radicals can be detected with this test.
- 3. Do not add more than two drops of cobalt nitrate, otherwise the residue obtained is black mass.
- Performing cobalt nitrate test with white residue left in the charcoal cavity test should be avoided. Instead, bore a fresh cavity and use the given mixture alone.

## 8.9.9.1 Chemistry of Cobalt Nitrate Test

Cobaltous oxide produced by the decomposition of cobalt nitrate combines with the metallic oxide formed to form 'double oxides' which have characteristics colours.

$$2\text{Co(NO}_3)_2 \longrightarrow 2\text{CoO} + \text{NO}_2 + \text{O}_2$$
Cobalt aitrate

Cobalt oxide

$$MgCO_3 \longrightarrow MgO + CO_2$$

Magnesium Magnesium carborate

$$2 \operatorname{ZnS} + 3O_2 \longrightarrow 2 \operatorname{ZnO} + 2 \operatorname{SO}_2$$

Zinc sulphide oxygen Zinc oxide Sulphur dioxide

i. 
$$CoO + ZnO \longrightarrow CoZnO_2$$
 (Cobalt zincate) or  $CoO \cdot ZnO$  Cobalt Zinc Green

oxide oxide

ii. 
$$CoO + Al_2O_3 \longrightarrow Co(AlO_2)_2$$
 or  $CoO \cdot Al_2O_3$ 

(Cobalt metaaluminate) Cobalt Aluminium Blue oxide oxide

#### 8.9.10 MICROCOSMIC SALT BEAD TEST

Sodium ammonium hydrogen phosphate tetrahydrate

(Na(NH<sub>4</sub>)H,PO<sub>4</sub>·4H<sub>2</sub>O, called microcosmic salt, gives on fusion a similar glassy, colourless bead as borax does. The salt on fusion is first dehydrated which then forms sodium meta-phosphate (NaPO<sub>3</sub>) as colourless bead which reacts with the metallic oxides giving coloured beads due to the formation of coloured orthophosphates. This test is suitable for Cu, Cr and Co, the colours for the corresponding metals being the same as for those of borax beads.

Table 8.10 Microcosmic salt bead test

Colour		Composition	Cation
1.	Blue bead with CuO	NaCuPO <sub>4</sub> sodium copper(II) orthophosphate	Cu <sup>2+</sup>
2.	Brown bead with CoO	NaCoPO <sub>4</sub> Sodium cobalt (II) orthophosphate	Co <sup>2+</sup>
3.	Green bead with $Cr_2O_3$	NaPO <sub>3</sub> .Cr <sub>2</sub> O <sub>3</sub>	Cr <sup>+3</sup>

#### 8.9.10.1 Chemical Reactions Involved

$$\begin{array}{c|c} Na(NH_4)\cdot HPO_4\cdot 4H_2O \xrightarrow{\Delta} NaPO_3 + NH_3 \uparrow + 5H_2O \\ & Sodium \\ & metaphosphate \\ \hline & NaCuPO_4 \xleftarrow{CuO} & CuO \\ & sodium \\ & copper(II) \\ & orthophosphate \\ & (blue) \\ \hline & Na.PO_3.Cr_2O_3 \\ & Sodium metaphosphate \\ & chromium(III) oxide. \\ & (Green) \\ \end{array}$$

Many silicates form a white translucent bead because they react with NaPO<sub>3</sub> and set free  $SiO_2$ , which remains undissolved in the bead. Thus this test is useful for the detection of silicates also. NaPO<sub>3</sub> + CaSiO<sub>3</sub>  $\longrightarrow$  NaCaPO<sub>4</sub> + SiO<sub>2</sub>

# 8.10 APPLICATIONS OF K<sub>sp</sub> IN QUALITATIVE SALT ANALYSIS

The separation and identification of various basic radicals into different group is mainly based upon six groups based on the increasing  $K_{\rm sp}$  values of corresponding precipitating compounds.

Group	Group reagent	Cations	Cations precipitated as
I.	Dilute HCl (2M) in cold	Hg <sub>2</sub> <sup>2+</sup> , Ag <sup>+</sup> , Pb <sup>2+</sup>	Hg <sub>2</sub> Cl <sub>2</sub> , AgCl, PbCl <sub>2</sub> (PbCl <sub>2</sub> is soluble in hot water, less in cold water
11.	H <sub>2</sub> S in presence of 0.2M HCl	II A: Hg <sup>2+</sup> , Pb <sup>2+</sup> , Bi <sup>3+</sup> , Cu <sup>2+</sup> , Cd <sup>2+</sup>	HgS, PbS, Bi <sub>2</sub> S <sub>3</sub> , CuS, CdS
Safety, 17		II B: As <sup>3+</sup> , As <sup>5+</sup> , Sb <sup>3+/+5</sup> Sn <sup>2+/4+</sup>	As <sub>2</sub> S <sub>3</sub> , As <sub>2</sub> S <sub>5</sub> , Sb <sub>2</sub> S <sub>3</sub> , Sb <sub>2</sub> S <sub>5</sub> , SnS, SnS <sub>2</sub>
ш.	NH <sub>4</sub> Cl + NH <sub>4</sub> OH	Fe <sup>3+</sup> , Cr <sup>3+</sup> ,	Fe(OH) <sub>3</sub> , Cr(OH) <sub>3</sub> , Al(OH) <sub>3</sub>
IV.	H <sub>2</sub> S in basic medium, i.e. H <sub>2</sub> S + NH <sub>4</sub> OH	Co <sup>2+</sup> , Ni <sup>2+</sup> , Mn <sup>2+</sup> , Zn <sup>2+</sup>	CoS, NiS, MnS, ZnS
<b>V.</b>	NH <sub>4</sub> Cl + NH <sub>4</sub> OH + (NH <sub>4</sub> ) <sub>2</sub> CO <sub>3</sub>	Ba <sup>2+</sup> , Sr <sup>2+</sup> , Ca <sup>2+</sup>	BaCO <sub>3</sub> , SrCO <sub>3</sub> , CaCO <sub>3</sub>
VI.	No specific reagent	$Na^{\oplus}, K^{\oplus}, Mg^{2^+}$	-
	Nessler's reagent in ammonical solution $K_2[HgI_4] + NH_4OH$	⊕ NH <sub>4</sub>	Iodide of Millon's base (Oxydimercuric ammonium iodide) OHgNH2

**Group I:** Dilute HCI is added to the solution containing cations. Since the  $K_{\rm sp}$  values of the chlorides of group I is less than  $K_{\rm sp}$  values of the chlorides of higher group, so only the chlorides of group I are precipitated.

If the concentrated HC1 is used, then  $[Cl^{\Theta}]$  will increase, then the ionic product  $(Q_{sp})$  of their chlorides will increase, so chlorides of other group may be precipitated. Moreover, PbCl<sub>2</sub> is soluble in conc. HCl.

**Group II:**  $H_2S_{(g)}$  is passed in an acidic medium to the solution containing cations. Since the  $K_{sp}$  values of the sulphides of group II ( $\approx 10^{-28}-10^{-54}$ ) is less than  $K_{sp}$  values of the sulphides of higher gp. (>10<sup>-28</sup>), so only the sulphides of group II are precipitated.  $H_2S$  is a weak acid and its dissociation can be suppressed to get low  $[S^{2-}]$  such that ionic products of group II sulphides are exceeded but not those of group III sulphides. This condition is achieved by passing  $H_2S$  in an acid medium so that  $H^{\oplus}$  (the common ion) suppress the dissociation of  $H_2S$ .

$$H_2S \Longrightarrow 2H^{\oplus} + S^{2-}$$
 $HCl \longrightarrow H^{\oplus} + Cl^{\Theta}$ 

Thus, the group II sulphides are precipitated but not of other groups under these conditions because their  $K_{\rm sp}$  values are quite high.

Note: pb<sup>2+</sup> is included in both groups I and II. PbCl<sub>2</sub> is sparingly while in dil. HCl. Any Pb<sup>2+</sup> ion present in group I filterate will spiritated as PbS in group II precipitated as PbS in group II.

III: Hydroxides of group III are precipitated by adding an of solid NH<sub>4</sub>Cl to the solutions of these cations followed whe addition of excess of NH<sub>4</sub>OH.

OH is a weak base and is slightly ionised, whereas NH<sub>4</sub>C1 whereas NH strong electrolyte, ionises almost completely to give we [NH4] ions.

$$\stackrel{\oplus}{\text{NH}_4\text{OH}} \Longrightarrow \stackrel{\oplus}{\text{NH}_4} + \stackrel{\odot}{\text{OH}} \qquad \qquad \text{NH}_4\text{Cl} \longrightarrow \stackrel{\oplus}{\text{NH}_4} + \text{Cl}^{\odot}$$

not common ion effect, the suppression of ionisation of HOH occurs and [OH] decreases appreciably. But even with  $\log_{10}$  [OH] ions, exceed the low value of the  $K_{\rm sp}$  of their adroxides. Hence, only the hydroxides of group III get respitated but not of other groups under these conditions because  $\int_{\mathbb{R}^n} K_{sn}$  of their hydroxides are quite high.

- 1. NaOH cannot be used in place of NH4OH being a strong base,  $[\stackrel{\odot}{OH}]$  will be high, and hence the hydroxides of the other group will precipitate out.
- 2. NH<sub>4</sub>OH should be added only after adding NH<sub>4</sub>Cl otherwise common ion effect would not occur in absence of NH<sub>4</sub>Cl. Hence, hydroxides of other group will be precipitated out.
- 3. NaCl and NaOH cannot be used in place of NH<sub>4</sub>Cl and NH<sub>4</sub>OH. Both being strong ionises completely to give high [OH]. NaCl cannot suppress the ionisation of NaOH. Therefore, hydroxides of other group will precipitate out. Moreover, Al(OH), and Cr(OH), are soluble in excess of NaOH because of the formation of aluminate and chromate, respectively.

Group IV: Precipitation of sulphides of group IV occurs in Presence of large excess of  $\mathrm{NH_4OH}$ .  $K_{\mathrm{sp}}$  of sulphides of group  $\mathbb{V}$  are sufficiently high. Therefore high concentration of  $S^{2-}$  ions  $^{\rm as}$  compared to that required in group II is needed for which  $K_{\rm sp}$ values are low).

H<sub>2</sub>S is weakly ionised as:

H<sub>2</sub>S 
$$\rightleftharpoons$$
 2H <sup>$\oplus$</sup>  + S<sup>2-</sup> NH<sub>4</sub>OH  $\rightleftharpoons$  NH<sub>4</sub> + OH

In presence of NH<sub>4</sub>OH, OH ions neutralise H<sup>⊕</sup> ions. According Le Chatelier's principle, ionisation of H<sub>2</sub>S proceeds in forward direction. Therefore, [S<sup>2</sup>] increases. Ultimately, the ionic products of the sulphides of group IV exceeds the  $K_{\rm sp}$  values of their corresponding metal sulphides and hence get precipitated.

Note: (NH<sub>4</sub>),SO<sub>4</sub> cannot be used in place of NH<sub>4</sub>OH, because the sulphates of Ba, Ca and Sr will get precipitated as white precipitate.

Group V: The carbonates of group V are precipitated by adding (NH<sub>4</sub>)<sub>2</sub>CO<sub>3</sub> solution to the solution of these cations in the presence of NH<sub>4</sub>Cl and NH<sub>4</sub>OH. (NH<sub>4</sub>)<sub>2</sub>CO<sub>3</sub> is a weak electrolyte that ionises slightly to give small [CO<sub>3</sub><sup>2-</sup>] ions.

$$(NH_4)_2CO_3 \Longrightarrow 2NH_4 + CO_3^{2-}$$

NH<sub>4</sub>Cl is a strong electrolyte, ionises almost completely to give large [NH<sub>4</sub>]. Due to the common ion effect, the dissociation of (NH<sub>4</sub>)<sub>2</sub>CO<sub>3</sub> is suppressed and hence high [CO<sub>3</sub><sup>2-</sup>] decreases considerably. But even with this low [CO<sub>3</sub><sup>2</sup>] ions, the ionic products of these cations and  ${\rm CO_3}^{2-}$  ions exceed the low  $K_{\rm sp}$  values of their corresponding metal carbonates and thus get precipitated.

Note: However, under these conditions, Mg salts do not get precipitated as MgCO3 since its Ksp value is comparatively high and thus requires a high [CO<sub>3</sub><sup>2</sup>] ions for precipitation. The carbonates of Na $^{\oplus}$ , K $^{\oplus}$  and  $\stackrel{\uplus}{N}H_4$  are also not precipitated because they are quite soluble.

The necessity of adding NH<sub>4</sub>OH arises due to the fact that (NH<sub>4</sub>)<sub>2</sub>CO<sub>3</sub> solution usually contains a large amount of NH<sub>4</sub>HCO<sub>3</sub>. Thus, the cations of group V will form not only insoluble carbonates but also soluble bicarbonates. As a result, the precipitation will not be complete. In order to convert NH<sub>4</sub>HCO<sub>3</sub>, NH₄OH is always added.

$$NH_4HCO_3 + NH_4OH \longrightarrow (NH_4)_2CO_3 + H_2O$$

#### Note:

- 1. Na<sub>2</sub>CO<sub>3</sub> cannot be used in place of (NH<sub>4</sub>)<sub>2</sub>CO<sub>3</sub> because Na<sub>2</sub>CO<sub>3</sub> is a strong electrolyte whose ionisation cannot be suppressed by common ion effect. Therefore, the large [CO<sub>3</sub><sup>2-</sup>] ions will also precipitate magnesium.
- 2. Large excess of NH<sub>4</sub>Cl should be avoided. Since the large excess of NH<sub>4</sub>Cl further reduces the [CO<sub>3</sub><sup>2-</sup>] ions, to such a low value that it even does not exceed the K<sub>sp</sub> values of group V radicals.
- 3. The solution should be warmed and not boiled while precipitating group V radicals. Since warming decomposes the soluble bicarbonates (impurities) of Ca, Sr and Ba into insoluble carbonates.

$$Ca(HCO_3)_2 \longrightarrow CaCO_3 + H_2O + CO_2$$

Boiling dissolves the insoluble carbonates as chlorides.

$$CaCO_3 + 2NH_4Cl \longrightarrow CaCl_2 + (NH_4)_2CO_3$$

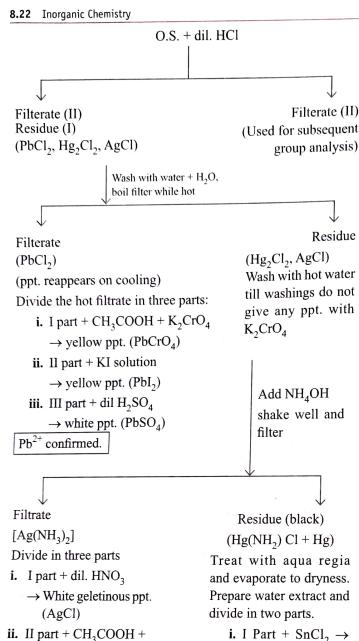
4. The group V precipitates should be dissolved in acetic acid. If the precipitates are dissolved in strong acid like HCl or HNO3. Ca will not get precipitated as calcium oxalate by adding ammonium oxalate because it is soluble in strong

H<sub>2</sub>SO<sub>4</sub> precipitates sulphates of Ca, Ba and Sr.

# 8.11 ANALYSIS OF GROUP I $(Ag^{\oplus}, Pb^{2+}, Hg_2^{2+})$

Group reagent is dil. HCl. Chlorides of Pb<sup>2+</sup>, Hg<sub>2</sub><sup>2+</sup>, Ag<sup>⊕</sup> are precipitated on addition of dil. HCl to solution of mixture (original solution)

(O.S.) + Filter.



(AgCl) ii. II part + CH<sub>3</sub>COOH +  $K_2$ CrO<sub>4</sub>  $\rightarrow$  Brick red ppt. (Ag<sub>2</sub>CrO<sub>4</sub>)

iii. III part + KI solution

→ Yellow ppt. (AgI)

Ag<sup>⊕</sup> confirmed.

- i. I Part +  $SnCl_2 \rightarrow$ Greyish white ppt. (Hg<sub>2</sub>Cl<sub>2</sub> + Hg)
- ii. II part + KI solution
  - → Yellow ppt. (HgI<sub>2</sub>) soluble in KI solution

Hg<sub>2</sub><sup>2+</sup> confirmed.

#### 8.11.1 CHEMICAL REACTIONS INVOLVED

 $Ag^{\oplus}$ ,  $Pb^{2+}$ ,  $Hg_2^{2+}$  are precipitated as insoluble chlorides on adding dil. HCl to aqueous solution. If no ppt. appears than group I is absent.

$$Ag + Cl^{\Theta} \longrightarrow AgCl \downarrow$$

$$Pb^{2+} + 2Cl^{\Theta} \longrightarrow PbCl_{2} \downarrow$$

$$Hg_{2}^{2+} + 2Cl^{\Theta} \longrightarrow Hg_{2}Cl_{2} \downarrow$$

- i. Filter the ppt. Filtetrate is used for identification of group II.
- ii. PbCl<sub>2</sub>(A) is soluble in hot water and thus separated.
- iii. AgCl is soluble in aqueous  $NH_3$  as  $[Ag(NH_3)_2]Cl$

$$AgCI + 2NH_3 \longrightarrow [Ag(NH_3)_2]CI$$
Diammine silver (I)
chloride (soluble), (B)

iv. Hg<sub>2</sub>Cl<sub>2</sub> is blackened by NH<sub>3</sub>

$$Hg_2Cl_2 + 2NH_3 \longrightarrow [H_2N.HgCl + Hg] + NH_4Cl$$
Black (C)

Pb<sup>2+</sup>:

A: Soluble PbCl<sub>2</sub> (in hot water) solution.

i. 
$$(A) + K_2CrO_4 \longrightarrow Yellow ppt.$$

$$PbCl_2 + K_2CrO_4 \longrightarrow PbCrO_4 \downarrow + 2KCl$$

$$Yellow$$

ii. (A) + KI 
$$\longrightarrow$$
 Yellow ppt.  
PbCl<sub>2</sub> + 2KI  $\longrightarrow$  PbI<sub>2</sub>  $\downarrow$  + 2KCl Yellow ppt.

iii. (A) + 
$$H_2SO_4 \longrightarrow White ppt.$$
  
 $PbCl_2 + H_2SO_4 \longrightarrow PbSO_4 \downarrow + 2HCl$   
White ppt.

Ag<sup>⊕</sup>:

B: Soluble [Ag(NH<sub>3</sub>)<sub>2</sub>]Cl

i. (B) + HNO<sub>3</sub> 
$$\longrightarrow$$
 White ppt.  
[Ag(NH<sub>3</sub>)<sub>2</sub>]Cl + 2HNO<sub>3</sub>  $\longrightarrow$  AgCl  $\downarrow$  + 2NH<sub>4</sub>NO<sub>3</sub>  
White ppt.

ii. (B) + 
$$K_2CrO_4$$
  $\longrightarrow$  brick red ppt.  
 $2[Ag(NH_3)_2]Cl + K_2CrO_4$   $\longrightarrow$   $Ag_2CrO_4 \downarrow + 2KCl + 2NH_3$   
Yellow ppt.

iii. (B) + KI 
$$\longrightarrow$$
 yellow ppt. 
$$[Ag(NH_3)_2]Cl + KI \longrightarrow Agl \downarrow + KCl + 2NH_3$$
Yellow ppt.

Hg<sub>2</sub><sup>2+</sup>:

Black  $[Hg(NH_2)Cl + Hg] + aqua regia and heat to dissolve the black ppt.$ 

i. Add  $SnCl_2 \longrightarrow White ppt.$  changing to grey.

ii. 
$$\underbrace{\text{HNO}_3(\text{conc.}) + 3\text{HCl}(\text{conc.})}_{\text{Aqua regia}} \xrightarrow{\Delta} \text{NOCl} + 2\text{H}_2\text{O} + 2[\text{Cl}]$$

# $_{ijl}$ $_{Hg(NH_2)Cl} + Hg + 2HCl + 2[Cl] \xrightarrow{\Delta} 2HgCl_2 + NH_4Cl$ $_{\text{W. 2HgCl}_2}$ + $\text{SnCl}_2 \longrightarrow \text{Hg}_2\text{Cl}_2 \downarrow + \text{SnCl}_4$

$$_{\text{V. }} \text{Hg}_2\text{Cl}_2 + \text{SnCl}_2 \longrightarrow 2\text{Hg} \downarrow + \text{SnCl}_4$$
Grey ppt.

$$HgCl_2 + KI \longrightarrow HgI_2 \downarrow + 2KCl$$
Yellow

$$\begin{array}{ccc} \operatorname{HgI}_2 + 2\operatorname{KI} & \longrightarrow & \operatorname{K}_2[\operatorname{HgI}_4] \\ & \operatorname{Grey \; ppt.} \end{array}$$

## LUSTRATION 8.5

Colourless salt (A) 
$$\xrightarrow{\text{dil. HCl}}$$
 White ppt. (B)
Soluble in H<sub>2</sub>O Soluble in hot water
$$\downarrow_{\text{(ii) FeSO}_4\text{(ii) conc. H}_2\text{SO}_4}$$
Brown colour ring (D) Yellow ppt. (C)

Identify (A), (B), (C) and (D).

(B): PbCl<sub>2</sub>

(D):  $[Fe(H_2O)_5NO]^{2+}$ 

#### LLUSTRATION 8.6

Identify (A), (B), (C) and (D) in the following:

Colourless salt (A) + conc.  $H_2SO_4 \longrightarrow Brown$  fumes intensified on adding Cu turnings.

Aqueous solution (A) + Cu  $\longrightarrow$  Blue coloured solution (B) and metal (C).

Aqueous solution (A) + HCl  $\longrightarrow$  White ppt. soluble in aqueous NH<sub>3</sub> forming (D).

(B):  $Cu(NO_3)_2$ 

(C): Ag

(D):  $[Ag(NH_3)_2Cl]$ 

#### ILLUSTRATION 8.7

Salt (A) makes part of electrode and is soluble in water. (A) is blackened by NH3 forming (B). (B) is soluble is aqua regia forming (C). (C) gives orange ppt. with KI but ppt. dissolves in excess of KI forming (D). Identify (A), (B), (C) and (D).

#### Sol.

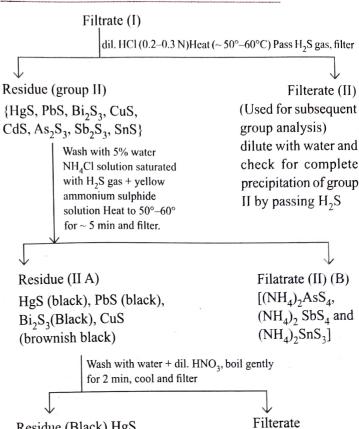
(A): Hg<sub>2</sub>Cl<sub>2</sub>(calomel)

(B):  $(HgNH_2Cl + Hg)$ 

(C): HgCl<sub>2</sub>

(D):  $K_2[HgI_4]$ 

## 8.12 ANALYSIS OF GROUP II



Residue (Black) HgS Treat it in the same way as in group I analysis

Residue (white, PbSO<sub>4</sub>)

 $(Pb(NO_3)_2, Bi(NO_3)_3,$  $Cu(NO_3)_2$ ,  $Cd(NO_3)_2$ dil. H,SO, Filtrate (nitrates and sulphates of  $Bi^{3+}$ ,  $Cu^{2+}$ ,  $Cd^{2+}$ ) Add excesas of NH,OH

CH<sub>3</sub>COH + K<sub>2</sub>CrO<sub>4</sub> Yellow ppt. (PbCrO<sub>4</sub>) Pb<sup>2+</sup> confirmed.

Dissolve in ammonium

acetate solution add

Residue (white, Bi(OH<sub>3</sub>)) Dissolve in minumum of dil. HCl, divide in three parts

- i. I part + excess of water
  - → Water turns milky
- ii. II part + Sodium stannite solution → Black ppt.
- iii. III part + Thiourea → Yellow colour

or ppt

Bi<sup>3+</sup> confirmed.

 $([Cu(NH_3)_4]^{2+}$  and  $[Cd(NH_3)_4]^{2+}$ If solution is coloureless Cu<sup>2+</sup> is absent; Cd<sup>2+</sup> may be present. Pass H<sub>2</sub>S gas yellow ppt. (CdS)

Filtrate

Cd<sup>2+</sup> confirmed.

If solution is blue, both Cd2+ and Cu<sup>2+</sup> may be present. Divide the solution in three parts.

- i. I Part + CH<sub>2</sub>COOH (till blue colour disappears) +  $K_4[Fe(CN)_6]$  Soln.
  - → Chocolate brown ppt.

Cu<sup>2+</sup> confirmed.

ii. II part + conc.  $HCl + Pass H_2S_{(g)}$ 

→ Black ppt. of CuS, filter and dilute the filtrate and pass H,S gas again → Yellow ppt. (CdS)

Both Cu<sup>2+</sup> and Cd<sup>2+</sup> confirmed.

iii. III part + KCN soln. (till blue colour disappeares)  $+H_2S \rightarrow \text{yellow ppt of CdS}$ 

Cd<sup>2+</sup> confirmed.

#### Filerate (II B)

(i) dil HCl, (ii) conc. HCl and boil for 5 min dilute with water (2-3 mL) and filter

Residue (yellow, As<sub>2</sub>S<sub>3</sub>) Dissolve in Divide in two parts

i. I part + excess of ammonium molybdate solution boil and cool → Canary yellow ppt.

As<sup>3+</sup> confirmed.

ii. II part + Boil to dryness.

Extract with NH<sub>4</sub>OH.

Add Mg(NO<sub>3</sub>)<sub>2</sub> solution, stir and allow to stand → White crystalline ppt  $[Mg(NH_A)AsO_A]$ In the ppt. and CH<sub>2</sub>COOH + AgNO<sub>2</sub> Red-brown ppt. of  $Ag_3AsO_4$ 

As<sup>3+</sup> confirmed.

Filterate (SbCl<sub>3</sub>, SnCl<sub>4</sub>) Boil off H2S gas Divide in three parts

i. I Part + Al wire (2–3 pieces) and warm gently for 5 min. Filter.

Filterate Residue, Add HgCl<sub>2</sub> Black, Sb<sup>3+</sup> solution  $\rightarrow$  greyish white ppt. Sn<sup>2+</sup> confirmed.

ii. II part + NH<sub>4</sub>OH (in excess) oxalic acid (solid). Warm and pass H<sub>2</sub>S gas. Filter.

**Filterate** 

Residue, Boil off H2S. Add orange, few drops of FeCl<sub>2</sub>  $Sb_2S_3$ + DMG solution + tartaric acid + NH₄OH (till basic) Red colouration.

Sn<sup>2+</sup> confirmed.

iii. III part + add excess of water → water becomes milky

Sb<sup>3+</sup> confirmed.

#### 8.12.1 CHEMICAL REACTIONS INVOLVED

Group II: Hg<sup>2+</sup>(mercuric),

II A:  $Pb^{2+}$ ,  $Bi^{3+}$ ,  $Cu^{2+}$ ,  $Cd^{2+}$ II B: As<sup>3+</sup>, Sb<sup>3+</sup>, Sn<sup>2+</sup>, Sn<sup>4+</sup> Group reagent: H<sub>2</sub>S<sub>(g)</sub> in presence of HCl

These radicals are precipitated as their sulphides while the sulphides of other metals remain in solution because of their high solubility product. HCl acts as a source of H<sup>®</sup> and thus decreases the concentration of  $S^{2-}$  (common-ion-effect). Hence, the decreased concentration of S<sup>2-</sup> is sufficient to precipitate the group II metals due to their low  $K_{\rm sp}$  values. (Group IV metals have high solubility products)

PbS, HgS, Bi<sub>2</sub>S<sub>3</sub>, CuS) (black); CdS, SnS<sub>2</sub>, As<sub>2</sub>S<sub>3</sub>) (yellow) Sb<sub>2</sub>S<sub>3</sub> (orange); SnS (brown)

1. PbS, CdS are precipitated in dilution only due to higher  $K_{sp}$ PbCl<sub>2</sub> Hot water Dissolved Cooling ppt of PbCl<sub>2</sub> reappears

$$Pb^{2+} + CrO_4^{2-} \longrightarrow PbCrO_4$$

$$Yellow$$

$$Pb^{2+} + SO_4^{2-} \longrightarrow PbSO_4$$

$$White$$

$$Pb^{2+} + OH^{\Theta} \longrightarrow Pb(OH)_2$$

$$White$$

$$VaOH (excess)$$

$$Na_2PbO_2 \xrightarrow{Oxidised} Na_2PbO_3$$

$$PbS + 3/2O_{2} \xrightarrow{300^{\circ}C} PbO + SO_{2}$$

$$Yellow$$
(Massicot)
$$PbO \xrightarrow{900^{\circ}C} PbO$$

Yellow (Massicot) Red (litharge)

- 2. IIA sulphides are insoluble in yellow ammonium sulphides and IIB sulphides are soluble in it.
- 3. HgS is insoluble in dilute HNO<sub>3</sub> while PbS, Bi<sub>2</sub>S<sub>3</sub>, CuS, CdS are soluble in it.
- 4. In water, Bi<sub>2</sub>S<sub>3</sub>, CuS, CdS etc are soluble to give respective hydroxides, but  $PbSO_4$  is not soluble.
- **5.** Hydroxides formed above in (4):

Bi(OH)<sub>3</sub> is insoluble in NH<sub>4</sub>OH.

Cu(OH)<sub>2</sub> and Cd(OH)<sub>3</sub> form soluble complexes.

 $Bi(SO_4)_3 + 6NH_4OH \longrightarrow 2Bi(OH)_3 \downarrow + 3(NH_4)_2SO_4$ 

 $\text{CuSO}_4 + 4\text{NH}_4\text{OH} \longrightarrow [\text{Cu(NH}_3)_4]\text{SO}_4 + 4\text{H}_2\text{O}$ (Deep blue)

 $[Cu(NH_3)_4]SO_4 + 4CH_3COOH \longrightarrow$ CuSO<sub>4</sub> + 4CH<sub>3</sub>COONH<sub>4</sub>

 $CuSO_4 + K_4[Fe(CN)_6] \longrightarrow Cu_2[Fe(CN)_6] \downarrow + 2K_2SO_4$ Red brown ppt.

 $CdSO_4 + 4NH_4OH \longrightarrow [Cd(NH_3)_4]SO_4 + 4H_2O$ (Colourless)

 $[Cd(NH<sub>3</sub>)<sub>4</sub>] SO<sub>4</sub> + H<sub>2</sub>S \longrightarrow CdS \downarrow + (NH<sub>4</sub>)<sub>2</sub> SO<sub>4</sub> + 2NH<sub>3</sub>$ 

Note: HgS is only sulphide of group II which does not dissolve in conc. HNO<sub>3</sub>

 $_{SO, aqua}$  regia (HCl + HNO $_3$ ) (3 : 1) is used to dissolve it.  $_{3HgS}$  + 6HCl + 2HNO $_3$   $\longrightarrow$  3HgCl + 2NO + 3S + 4H $_2$ O  $_{Black}$ 

(Nessler's reagent)

1. 
$$HgCl_2 + 2KI \longrightarrow HgI_2 + 2KCl$$
  
Scarlet red ppt.  
 $Kl$   
 $K_2[HgI_4]$ 

2. 
$$2\text{HgCl}_2 + \text{SnCl}_2 \longrightarrow \text{Hg}_2\text{Cl}_2 + \text{SnCl}_4$$

White ppt.

$$\downarrow \text{SnCl}_2$$

$$2\text{Hg} + \text{SnCl}_4$$
Black ppt.

Tests for Pb2+:

1. 
$$Pb(NO_3)_2 + K_2SO_4 \longrightarrow PbSO_4 + 2KNO_3$$
  
White

PbSO<sub>4</sub> is soluble in ammonium acetate

$$PbSO_4 + 2CH_3COONH_4 \longrightarrow (NH_4)_2SO_4 + (CH_3COO)_2Pb$$

2. 
$$Pb(NO_3)_2 + K_2CrO_4 \longrightarrow PbCrO_4 + 2KNO_3$$
  
Yellow ppt

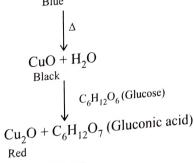
$$Na_2PbO_2 + Na_2CrO_4 + 2H_2O$$

Yellow soln.

Tests for Cu<sup>2+</sup>:

1. 
$$2\text{Cu(NO}_3)_2 + \text{K}_4[\text{Fe(CN)}_6] \longrightarrow \text{Cu}_2[\text{Fe(CN)}_6] + 4\text{KNO}_3$$
  
Chocolate brown ppt.

2. 
$$Cu(NO_3)_2 + 2NaOH \longrightarrow Cu(OH)_2 + 2NaNO_3$$



3. 
$$Cu(NO_3)_2 + 2KI \longrightarrow CuI_2 + 2KNO_3$$
Brown

$$K_{3}[CuI_{4}] \stackrel{3KI}{\longleftarrow} \frac{1}{2} Cu_{2}I_{2} + I_{2} \stackrel{KI}{\longrightarrow} KI_{3}$$
Yellow ppt. Violet

4. 
$$2Cu(NO_3)_2 + 2Na_2S_2O_3 \longrightarrow Cu_2(NO_3)_2 + Na_2S_4O_6 + 2NaNO_3$$

$$Cu_{2}(NO_{3})_{2} + Na_{2}S_{2}O_{3} \longrightarrow Cu_{2}(S_{2}O_{3}) + 2NaNO_{3}$$
White
$$\downarrow Na_{2}S_{2}O_{3}$$

$$\downarrow^{+4} +1 \times 6 \qquad -2 \times 5 \qquad Na_{4}[Cu_{6}(S_{2}O_{3})_{5}]^{-4} (465 \text{ complex})$$
For remembrance
$$\downarrow A \qquad 6 \qquad 5 \qquad 465 \text{ complex}$$

$$\downarrow Na \qquad Cu \qquad S_{2}O_{2} \qquad 465 \text{ complex}$$

**5.** Bi(OH)<sub>3</sub> is soluble in dilute HCl to form BiCl<sub>3</sub> which is tested in two ways.

Bi(OH)<sub>3</sub> + 3HCl 
$$\longrightarrow$$
 BiCl<sub>3</sub> + 3H<sub>2</sub>O  
**a.** BiCl<sub>3</sub> + H<sub>2</sub>O  $\longrightarrow$  BiOCl $\downarrow$  + 2HCl  
White ppt  
(oxychloride)

**b.** 
$$2\text{BiCl}_3 + 2\text{Na}_2\text{SnO}_2 + 6\text{NaOH} \longrightarrow$$
  
 $2\text{Bi} \downarrow + 3\text{Na}_2\text{SnO}_3 + 6\text{NaCl} + 3\text{H}_2\text{O}$   
Black

- Arsenic sulphides is insoluble in conc. HCl while Sb, Sn sulphides are soluble. Sb<sub>2</sub>S<sub>3</sub> can be precipitated in presence of oxalic acid.
- 7. Cu and Cd separation is based on fact that in presence of KCN, only Cd is precipitated as sulphides on passing H<sub>2</sub>S.

Effect of heat:

CuSO<sub>4</sub>·5H<sub>2</sub>O Exposure CuSO<sub>4</sub>·5H<sub>2</sub>O
Blue
$$\begin{array}{c}
\text{CuSO}_4 \cdot 5\text{H}_2\text{O} \\
\text{Blue}
\end{array}$$
CuSO<sub>4</sub>·4H<sub>2</sub>O
Bluish white
$$\begin{array}{c}
\text{230°C} \\
\text{Black}
\end{array}$$
White
$$\begin{array}{c}
\text{1100°C} \\
\text{Red}
\end{array}$$

Tests for Cd<sup>2+</sup>:

$$3CdS + 8HNO_3 \longrightarrow 3Cd(NO_3)_2 + 3S + 4H_2O$$
  
Yellow

$$1..2\text{Cd(NO}_3)_2 + \text{K}_4[\text{Fe(CN)}_6] \longrightarrow \text{Cd}_2[\text{Fe(CN)}_6] + 4\text{KNO}_3$$
Blue/White

2. 
$$Cd(NO_3)_2 + 2NaOH \longrightarrow 2NaNO_3 + Cd(OH)_2$$
 White

$$H_2O + CdO$$
 Brown

3. 
$$Cd(NO_3)_2 + 2NH_4OH \longrightarrow Cd(OH)_2 + 2NH_4NO_3$$

$$\downarrow 2NH_4OH \atop (excess)$$

$$[Cd(NH_3)_4](NO_3)_2 + 4H_2O$$
  
2NH + 2NH NO + CdS (

 $2NH_3 + 2NH_4NO_3 + CdS \leftarrow Yellow$ 

4. 
$$Cd(NO_3)_2 + 2KCN \longrightarrow Cd(NO_3)_2 + 2KCN$$

$$| KCN | KCN |$$

$$2HCN + 2KCN + CdS \xleftarrow{H_2S}_{Yellow} K_3[Cd(CN)_4]_{Soluble Complex}$$

#### Tests for As<sup>3+</sup>:

As<sub>2</sub>S<sub>3</sub> (Soluble in ammonium sulphide)
Yellow

#### Tests for Sb<sup>3+</sup>:

1. 
$$Sb_2S_3 + 2(NH_4)_2S_2 \longrightarrow Sb_2S_5 + 2(NH_4)_2S$$
Orange
Orange

2. 
$$SbCl_3 + H_2O \longrightarrow SbOCl + 2HCl$$
White turbidity

3. 
$$SbCl_3 + 3H_2S \longrightarrow Sb_2S_3 + 6HCl$$
Orange

#### Tests for Sn<sup>2+</sup> and Sn<sup>4+</sup>:

$$\begin{array}{c} \operatorname{SnS} + (\operatorname{NH_4})_2\operatorname{S}_2 \longrightarrow \operatorname{SnS_2} + (\operatorname{NH_4})_2\operatorname{S}_2 \\ \operatorname{Yellow} \\ & \sqrt{(\operatorname{NH_4})_2\operatorname{S}_2} \\ & (\operatorname{NH_4})_2\operatorname{SnS_3} \text{ (Soluble)} \\ \operatorname{SnS_2} + \operatorname{4HCl} \longrightarrow \operatorname{SnCl_4} + \operatorname{2H_2S} \\ \operatorname{SnCl_4} + \operatorname{Fe} \longrightarrow \operatorname{FeCl_2} + \operatorname{SnCl_2} \\ & \sqrt{\operatorname{HgCl_2}} \\ \operatorname{Hg_2Cl_2} + \operatorname{SnCl_4} \\ \operatorname{White} \\ & \overline{\operatorname{SnCl_4}} + \operatorname{SnCl_4} \\ \operatorname{Grey/Black} \end{array}$$

$$SnCl_4 + 2NH_4Cl \longrightarrow (NH_4)_2SnCl_6$$
Pink

**Note:** (NH<sub>4</sub>)<sub>2</sub>SnCl<sub>6</sub> or pink salt is used as mordant which holds the dyes in clothes.

# Analysis of both Cu<sup>2+</sup> and Cd<sup>2+</sup> present in the given mixture:

- 1. By fractional precipitation of Cu and Cd (using H<sub>2</sub>S gas):
- 2. Solution ([Cu(NH<sub>3</sub>)<sub>4</sub>]SO<sub>4</sub> and [Cd(NH<sub>3</sub>)<sub>4</sub>]SO<sub>4</sub> + conc. HCl  $\xrightarrow{\text{Pass H}_2\text{S gas}}$  black ppt. (CuS).

Filter. Dilute the filterate using water and pass  $H_2S$  gas  $\longrightarrow$  yellow ppt. (CdS).

This test is based on the difference in solubility product of CuS  $(8.5 \times 10^{-45})$  and CdS  $(3.6 \times 10^{-29})$ . When  $H_2S(g)$  is passed in presence of conc. HCl, only copper precipitates out. On dilution, the concentration of HCl decreases, enabling precipitation of CdS.

**2. KCN test:** When filterate is blue, addition of excess of KCN forms soluble colourless complexes with Cu and Cd respectively.

$$[Cu(NH3)4]SO4 + 10KCN \longrightarrow 2K3[Cu(CN)4] + 2K2SO4+ (CN)2 \uparrow + 8NH3 \uparrow$$

 $[Cd(NH_3)_4]SO_4 + 4KCN \longrightarrow K_2[Cd(CN)_4] + K_2SO_4 + 4NH_3$ The cyanogen  $(CN)_2$  produced reacts with the solution.

$$(CN)_2 + 2NH_3 + H_2O \longrightarrow NH_4CNO + NH_4CN$$

In cyanide complex copper is more stable than cyanide complex of cadmium. The primary ionisation of both complexes is as under:

$$K_3[Cu(CN)_4] \Longrightarrow 3K^{\oplus} + [Cu(CN)_4]^{3-}$$
  
 $K_3[Cd(CN)_4] \Longrightarrow 3K^{\oplus} + [Cd(CN)_4]^{3-}$ 

The secondary ionisation and ionisation constant of these

$$[Cu(CN)_4]^{3-} \rightleftharpoons Cu^{\oplus} + 4 CN^{\ominus} \qquad K = 5 \times 10^{-28}$$

$$[Cd(CN)_4]^{3-} \rightleftharpoons Cd^{\oplus} + 4CN^{\ominus} \qquad K = 1.4 \times 10^{-17}$$

With  $K_3[Cu(CN)_4]$ , the concentration of  $Cu^{\oplus}$  ions produced by the secondary ionisation of the complex into  $[Cu(CN)_4]^{3-}$  is insufficient to exceed the solubility product of  $Cu_2S$  on passing  $H_2S$ , hence no precipitation occurs. Whereas, secondary ionisation of  $K_3[Cd(CN)_4]$ , is comparatively high, therefore enough  $Cd^{\oplus}$  ions are available in the soluble and when  $H_2S$  gas is passed, yellow ppt. of CdS is obtained.

In this way Cd<sup>2+</sup> can be identified in presence of Cu<sup>2+</sup> ions.

#### ILLUSTRATION 8.8

complexes are:

If Cu<sup>2+</sup> and Cd<sup>2+</sup> both are present, it is difficult to analyse. Outline a scheme to analyse in a mixture.

Sol. KCN forms complex with Cu<sup>2+</sup> and Cd<sup>2+</sup>

$$Cu^{2+} + KCN \longrightarrow K_2[Cu(CN)_4]$$
Stable

$$Cd^{2+} + KCN \longrightarrow K_2[Cd(CN)_4]$$
Unstable

When  $H_2S$  gas is passed, unstable complex of  $Cd^{2+}$  gives yellow ppt.

$$[Cd(CN)_4]^{2-} = Cd^{2+} + 4CN^{\Theta}, \qquad Cd^{2+} + S^{2-} \longrightarrow CdS \downarrow$$
Yellow

#### ILLUSTRATION 8.9

HgS is soluble in aqua regia forming HgCl<sub>2?</sub> What happens if Cu turnings are added to HgCl<sub>2</sub>?

**Sol.**  $HgCl_2 + Cu \longrightarrow CuCl_2 + Hg$ . Hg is deposited on Cu.

#### ILLUSTRATION 8.10

Identify (A), (B), (C), (D) and (E). (A) (black) + dil. HC1  $\xrightarrow{\Delta}$  (B) (solution) + (C) (gas). Gas (C) turns lead acetate paper black. (B) gives orange ppt. (D) soluble in excess of KI forming (E).

**Sol.** (A): HgS, (B): HgCl<sub>2</sub>, (C): H<sub>2</sub>S, (D): HgI<sub>2</sub>, (E): K<sub>2</sub>HgI<sub>4</sub>

# LUSTRATION 8.11

one into solution white turbidity and into solution HCl, yellowish white turbidity appears. What do you dil. What precautions are taken to check this turbidity?

This yellowish white turbidity is due to colloidal sulphur, by oxidation of H<sub>2</sub>S by the presence of NO<sub>3</sub> or NO<sub>2</sub>

$$H_2S + HNO_3 \longrightarrow S \text{ (colloidal)}$$

passing H<sub>2</sub>S gas, solution is boiled so as to decompose radicals.

# LUSTRATION 8.12

(Arsenic group) sulphides are soluble in YAS. If conc. HCl is added to this soluble portion, coloured ppt. are formed. Write reactions.

$$(NH_4)_3AsS_4 + 6HC1 \longrightarrow As_2S_5 \downarrow + 6NH_4C1 + 3H_2S$$
Soluble

$$(NH_4)_2SnS_3 + 2HCl \longrightarrow SnS_2 \downarrow + 2NH_4Cl + H_2S$$

## 8.13 REMOVAL OF INTERFERING **RADICALS**

h a china-dish, add centrifugate of group II, boil off H<sub>2</sub>S gas check for the complete removal of H<sub>2</sub>S gas by using lead acetate paper)  $\longrightarrow$  solution (1).

a. When  $BO_3^{3-}$  or  $F^{\odot}$  is present: In the above solution (1), add conc. HCl, boil to dryness, repeat this process for 2-3 times. Add water (distilled) and proceed for the analysis of group III radicals

$$H^{\oplus} + BO_3^{3-} \longrightarrow H_3BO_3^{\uparrow}; \quad H^{\oplus} + F^{\ominus} \longrightarrow HF^{\uparrow}$$

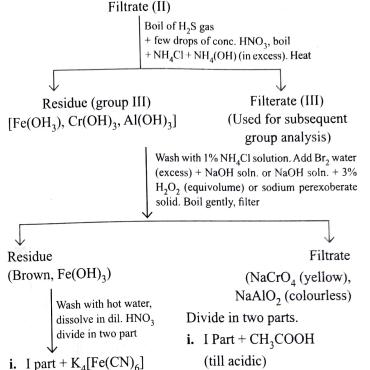
- b. When  $C_2O_4^{\ 2-}$  is present: In the solution (1), add conc. HNO<sub>3</sub>, boil to dryness repeat this process for 2-3 times. Add distilled water and proceed for the analysis of group III radicals.
- c. When  $PO_3^{3-}$  is present: In the solution (1), add dil. HCl (Normality should not exceed 1N), add NH<sub>4</sub>Cl solid, till it is dissolved. Add 2-3 drops of zirconyl nitrate reagent or zirconium nitrate reagent. White ppt. obtained is rejected. Repeat this process. Take the centrifugate obtained for the analysis of group III radicals.

$$ZrO(NO_3)_2 + 2Na_2HPO_4 + 2HCl \longrightarrow ZrO(H_2PO_4)_2 + 2NaCl + 2NaNO_3$$

or
$$ZrO(NO_3)_2 + Na_2HPO_4 \longrightarrow ZrO(HPO_4) + 2NaNO_3$$

## 8.14 ANALYSIS OF GROUP III

$$(Fe^{3+}, Al^{3+}, Cr^{3+})$$



- - → Prussian blue colour or ppt.
- ii. II part + NH₄SCN soln.
  - → Blood red colouration.

Fe<sup>3+</sup> confirmed.

# ii. II part + AgNO<sub>3</sub>

 $\rightarrow$  Brick red ppt (Ag<sub>2</sub>CrO<sub>4</sub>)

Cr3+ confirmed.

+ lead acetate soln.

Cr3+ confirmed.

→ Yellow ppt (PbCrO<sub>4</sub>)

#### 8.14.1 CHEMICAL REACTIONS INVOLVED

Boil off H<sub>2</sub>S from the filtrate of group II. Add NH<sub>4</sub>Cl and one drop of dil.  $HNO_3$ ; heat, cool and add  $NH_4OH \longrightarrow ppt$ .

- i. Reddish brown ppt. of Fe(OH)<sub>3</sub> if Fe<sup>3+</sup> is present (salt is brown).
- ii. Dirty green ppt. of Cr(OH), if Cr<sup>3+</sup> is present (salt is green).
- iii. White ppt. of Al(OH)<sub>3</sub> if Al<sup>3+</sup> is present (salt is colourless).
- iv. Dil. HNO<sub>3</sub> is added to oxidise Fe<sup>2+</sup> (light green) into Fe<sup>3+</sup> (deep yellow).
- v. NH<sub>4</sub>Cl by common ion effect decreases ionisation of NH₄OH.

Fe<sup>3+</sup>:

i. Fe(OH)<sub>3</sub> ppt. are insoluble in NaOH but soluble in conc. HCl/dil. HNO3

$$Fe(OH)_3 + 3HCl \longrightarrow FeCl_3 + 3H_2O$$
Soluble (A)

or 
$$Fe(OH)_3 + 3HNO_3 \longrightarrow Fe(NO_3)_3 + 3H_2O$$

$$(A) + CH_3COOH + K_4[Fe(CN)_6] \longrightarrow blue ppt.$$
Potassium
(Prussian blue)
ferrocyanide

$$4 \operatorname{FeCl}_{3} + 3K_{4}[\operatorname{Fe(CN)}_{6}] \longrightarrow \operatorname{Fe}_{4}[\operatorname{Fe(CN)}_{6}]_{3} + 12KCI$$
Ferric ferrocyanide
(Prussian blue)

$$FeCl_3 + NH_4SCN \longrightarrow [Fe(SCN)]Cl_2 + NH_4Cl$$

Blood red
colour

 $Fe^{2+}$  does not give these tests, hence at the start of the group,  $HNO_3$  is added to oxidise  $Fe^{2+}$  to  $Fe^{3+}$ .

Cr3+:

i. Cr(OH)<sub>3</sub> (green ppt.) are insoluble in NaOH but dissolve in presence of Br<sub>2</sub> water (oxidising agent) giving yellow coloured Na<sub>2</sub>CrO<sub>4</sub> solution.

$$Br_2 + H_2O \longrightarrow 2HBr + [O]$$
  
 $4NaOH + 2Cr(OH)_3 + 3[O] \longrightarrow 2Na_2CrO_4 + 5H_2O$   
Soluble (B)

ii. (B) + 
$$CH_3COOH + (CH_3COO)_2Pb \longrightarrow yellow ppt.$$

 $2\text{Na}_2\text{CrO}_4 + (\text{CH}_3\text{COO})_2\text{Pb} \longrightarrow \text{PbCrO}_4 \downarrow + 2\text{CH}_3\text{COONa}$ Yellow ppt.

iii. (B) + 
$$AgNO_3 \longrightarrow brick red ppt$$
.

$$Na_2CrO_4 + 2 AgNO_3 \longrightarrow 2NaNO_3 + Ag_2CrO_4 \downarrow$$
Brick red ppt.

Al<sup>3+</sup>:

i. White ppt. of Al(OH)<sub>3</sub> (salt is colourless) + NaOH solution (excess) → ppt. dissolves forming NaAlO<sub>2</sub>.

$$Al(OH)_3 + NaOH \longrightarrow 2H_2O + NaAlO_2$$
  
Sodium  
meta-aluminate  
(C) soluble

ii. White ppt. reappears if NH<sub>4</sub>Cl is added into soluble metaaluminate and boiled.

$$\begin{aligned} \mathrm{NH_4Cl} + \mathrm{NaAlO_2} + \mathrm{H_2O} &\longrightarrow \mathrm{NaCl} + \mathrm{Al(OH)_3} + \mathrm{NH_3} \\ \mathrm{(A)} & \mathrm{White\ ppt.} \end{aligned}$$

#### ILLUSTRATION 8.13

Light green solution of (A) does not give blue coloured ppt. with  $K_4[Fe(CN)_6]$  but on adding a drop of HNO<sub>3</sub>, blue ppt. (B) appears. However, (A) gives blue colour (C) with  $K_3[Fe(CN)_6]$ . Explain the formation of (B) and (C). Identify (A) if (A) also gives white ppt. with AgNO<sub>3</sub> solution.

Sol. (A): FeCl<sub>2</sub>

(B): KFe<sup>III</sup> [Fe<sup>II</sup>(CN)<sub>6</sub>], Prussian blue

(C): KFe<sup>II</sup> [Fe<sup>III</sup>(CN)<sub>6</sub>], Turnbull's blue

#### ILLUSTRATION 8.14

Identify (A), (B), (C) and (D) and explain reactions.

(A) (green coloured salt) +  $K_2Cr_2O_7$  + conc.  $H_2SO_4 \xrightarrow{\Delta}$  (B)

(B) (reddish brown gas) + NaOH → (C)(yellow coloured solution)

(C)  $+ (CH_3COO)_2Pb \longrightarrow (D)$  (yellow ppt.)

(A) + NaOH + Br<sub>2</sub> water  $\xrightarrow{\Delta}$  (C)

(C) +  $(CH_3COO)_2Pb \xrightarrow{\Delta} (D)$ 

Sol. (A): CrCl<sub>3</sub>

(B): CrO<sub>2</sub>Cl<sub>2</sub> [by chromyl-chloride test of Cl<sup>Θ</sup>]

(C): Na<sub>2</sub>CrO<sub>4</sub>

(D): PbCrO<sub>4</sub>

#### ILLUSTRATION 8.15

- a. (A) (yellow coloured solution) changes to light green coloured solution (B) on passing H<sub>2</sub>S gas. (A) and (B) both give white ppt. with BaCl<sub>2</sub> solution, insoluble in conc. HCl. (A) gives blue coloured ppt. (C) with K<sub>4</sub>[Fe(CN)<sub>6</sub>]. B does not. What are (A), (B) and (C)?
- **b.** Identify A, B, C and D in the following reactions: Bauxite + Charcoal +  $Cl_2 \xrightarrow{\Delta} A + CO$   $A + H_2O \longrightarrow B + HCl;$   $B + H_2SO_4 \longrightarrow C + H_2O$  $B + NaOH \longrightarrow D + H_2O$

#### Sol.

a. (A): FeCl<sub>3</sub> (B): FeCl<sub>2</sub>
 (C): KFe<sup>III</sup> [Fe<sup>II</sup>(CN)<sub>6</sub>], Prussian blue

b. 
$$Al_2O_3 + 3C + 3Cl_2 \xrightarrow{\Delta} 2AlCl_3 + 3CO$$
Bauxite

 $AlCl_3 + 3H_2O \xrightarrow{} Al(OH)_3 + 3HCl$ 
(A)

 $2Al(OH)_3 + 3H_2SO_4 \xrightarrow{} Al_2(SO_4)_3 + 6H_2O$ 
(B)

 $(C)$ 
 $Al(OH)_3 + NaOH \xrightarrow{} NaAlO_2 + 2H_2O$ 

# 15 ANALYSIS OF GROUP IV

Filtrate (III)  $NH_4OH + NH_4Cl$ Pass H<sub>2</sub>S gas

Residue (Brown)

 $(MnO_2 \cdot xH_2O)$ 

Dissolve in

conc. HNO,

in two parts.

i. I Part +  $H_2O_2$ ,

boil and cool.

Add sodium

bismuthate

solid. Stir.

 $(HMnO_{\Delta})$ 

allow to settle

 $\rightarrow$  Purple soln.

Boil and cool

→ Purple soln.

Mn<sup>2+</sup> confirmed.

Mn<sup>2+</sup> confirmed.

ii. II part +  $\overline{PbO_{\gamma}}(s)$ .

and divide

(Centrifugate (IV) Used for subsequent group analysis)

Residue (group IV) (CoS, NiS, ZnS, MnS)

dil. HCl, shake well, allow to stand, filter

**Filtrate** 

Filtrate

 $(Na, ZnO_2)$ 

Divide in two parts

 $\rightarrow$  white ppt. (ZnS)

Zn<sup>2+</sup>confirmed.

→ bluish white ppt.

+ pass H<sub>2</sub>S

ii. II part +

CH<sub>3</sub>COOH

 $+ K_4 Fe(CN)_6$ 

Zn<sup>2+</sup>confirmed.

i. I Part + CH<sub>3</sub>COOH

Residue Black, NiS and CoS)

(MnCl<sub>2</sub>, ZnCl<sub>2</sub>) Boil to expel H<sub>2</sub>S gas cool. Add NaOH soln. (excess) + H<sub>2</sub>O<sub>2</sub> soln. Boil and filter

evaporate to dryness. extract with water

Treat with aqua regia,

Divide in three parts. i, I part + NH4OH

+DMG soln. → Scarlet red ppt.

Ni<sup>2+</sup> confirmed.

ii. II part + CH3COOH

+KNO2 soln.

→ Yellow ppt.

Co<sup>2+</sup> confirmed.

iii. Palit's test III part +

NaHCO<sub>2</sub>(s)

+Br, water.

Shake.

a. Cold-Apple

green colour

Hot-No change

Only Co<sup>2+</sup>confirmed.

b. Cold-Apple green

colour Hot — Soln.

blackens.

Both Co<sup>2+</sup>, Ni<sup>2+</sup> confirmed.

c. Cold-No green colour Hot-Soln, blackens

Ni<sup>2+</sup> confirmed.

# <sup>8,</sup>15.1 Chemical Reactions Involved

Filtrate of group III + NH<sub>4</sub>OH + NH<sub>4</sub>Cl  $\xrightarrow{\Delta}$  Pass H<sub>2</sub>S gas

- i. White ppt. (salt colourless) of ZnS
- ii. Buff coloured ppt. (salt light pink) of MnS

iii. Black ppt. (salt green) of NiS

iv. Black ppt. (salt dark brownish black) of CoS

v. Addition of ammonia (i.e. conc. NH<sub>4</sub>OH) converts these cations except Mn<sup>2+</sup> into soluble amino complexes.

$$Zn^{2+} + 4NH_3 \longrightarrow [Zn(NH_3)_4]^{2+}$$
  
 $Co^{2+} + 6NH_3 \longrightarrow [Co(NH_3)_6]^{2+}$   
 $Ni^{2+} + 6NH_3 \longrightarrow [Ni(NH_3)_6]^{2+}$ 

vi. The ammoniacal solution containing Mn<sup>2+</sup> and these amino complexes get converted into sulphides when H<sub>2</sub>S is passed.

$$Mn^{2+} + S^{2-} \longrightarrow MnS \downarrow$$

Buff coloured

$$[Zn(NH_3)_4]^{2^+} + S^{2^-} \longrightarrow ZnS \downarrow + 4NH_3$$

$$(White ppt.)$$

$$[Co(NH_3)_6]^{2^+} + S^{2^-} \longrightarrow CoS \downarrow + 6NH_3$$

$$Blck ppt.$$

$$[Ni(NH_3)_6]^{2^+} + S^{2^-} \longrightarrow NiS \downarrow + 6NH_3$$

$$Blck ppt.$$

$$Blck ppt.$$

$$Blck ppt.$$

vii. Ammoniacal medium increases ionisation of H<sub>2</sub>S, hence higher  $[S^{2-}]$  will precipitate  $Zn^{2+}$ ,  $Co^{2+}$ ,  $Ni^{2+}$ ,  $Mn^{2+}$  as sulphides (having higher  $K_{\rm sp}$  values).

viii. In dil. HCl, NiS and CoS are insoluble, whereas MnS and ZnS are soluble.

$$MnS + 2HCl \longrightarrow MnCl_2 + H_2S$$
  
 $ZnS + 2HCl \longrightarrow ZnCl_2 + H_2S$ 

Ni<sup>2+</sup>:

i. NiS is soluble in aqua regia (3 parts of conc. HCl and 1 part of conc. HNO<sub>3</sub>)

$$3NiS + 2HNO_3 + 6HCl \longrightarrow 3NiCl_2 + 2NO + 3S + 4H_2O$$
  
Soluble  
(green) (A)

or in conc. HCl in presence of oxidising agent like KIO,

NiS + 2HCl + [O] 
$$\longrightarrow$$
 NiCl<sub>2</sub> + H<sub>2</sub>O + S  
conc. Soluble  
(green) (A)

ii. (A) +  $NH_4OH$  + dimethylglyoxime  $\longrightarrow$  scarlet red ppt.

NiCl<sub>2</sub> + 2 
$$\begin{pmatrix} CH_3 - C = NOH \\ CH_3 - C = NOH \\ dimethyl glyoxime \end{pmatrix}$$
 + NH<sub>4</sub>OH  $\begin{pmatrix} CH_3 - C = NOH \\ dimethyl glyoxime \end{pmatrix}$  + NH<sub>4</sub>OH  $\begin{pmatrix} CH_3 - C = N \\ CH_3 - C = N \\ CH_3 - C = N \end{pmatrix}$  Ni  $\begin{pmatrix} N = C - CH_3 \\ N = C - CH_3 \\ O \end{pmatrix}$  + 2NH<sub>4</sub>Cl + 2H<sub>2</sub>Cl  $\begin{pmatrix} CH_3 - C = NOH \\ CH_3 - C = NOH \\ O \end{pmatrix}$  Scarlet red ppt. (dimethyl glyoximate)

 $Co^{2+}$ :

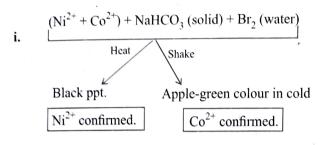
Co<sup>2+</sup> is soluble in aqua regia forming CoCl<sub>2</sub> (B)

$$3CoS + 2HNO_3 + 6HCl \longrightarrow 3CoCl_2 + 2NO + 3S + 4H_2O$$
Soluble (B)

or in conc. HCl in presence of oxidising agent like  ${\rm KIO_3}$  $CoS + 2HCl + [O] \longrightarrow CoCl_2 + H_2O + S$ 

(B) + CH<sub>3</sub>COOH + KNO<sub>2</sub> 
$$\longrightarrow$$
 yellowish orange ppt.  
CoCl<sub>2</sub> + 2KNO<sub>2</sub>  $\longrightarrow$  2KCl + Co(NO<sub>2</sub>)<sub>2</sub>  
CH<sub>3</sub>COOH + KNO<sub>2</sub>  $\longrightarrow$  CH<sub>3</sub>COOK + HNO<sub>2</sub>  
II  
Co(NO<sub>2</sub>)<sub>2</sub> + 2HNO<sub>2</sub>  $\longrightarrow$  K<sub>3</sub>[Co(NO<sub>2</sub>)<sub>6</sub>]  
Potassium cobaltinitrite  
(yellowish orange ppt.)

Palit's test: Co<sup>2+</sup> and Ni<sup>2+</sup> can be analysed in presence of each other as follows:



ii. 
$$CoCl_2 + NaHCO_3 + NaOH \longrightarrow 2NaCl + CoCO_3 + H_2O$$
  
 $2NaHCO_3 + NaOH \xrightarrow{\Delta} Na_2CO_3 + H_2O + CO_2$   
 $CoCO_3 + 2Na_2CO_3 \xrightarrow{\Delta} Na_4[Co^{ll} (CO_3)_3]$   
 $2Na_4[CoCO_3)_3] + 2NaHCO_3 + O \xrightarrow{\Delta}$   
 $2Na_3[Co^{lll} (CO_3)_3] + 2Na_2CO_3 + H_2O$   
(Apple-green)  
sodium cobalticarbonate

iii. 
$$\text{NiCl}_2 + 2\text{NaHCO}_3 \xrightarrow{\Delta} \text{NiCO}_3 + 2\text{NaCl} + \text{H}_2\text{O} + \text{CO}_2$$
  
 $\text{Br}_2 + \text{H}_2\text{O} \xrightarrow{\Delta} \text{HBr} + [\text{O}]$   
 $2\text{NiCO}_3 + 4\text{NaOH} + [\text{O}] \xrightarrow{\Delta} \text{Ni}_2\text{O}_3 + 2\text{Na}_2\text{CO}_3 + \text{H}_2\text{O}$   
Black

iv. Mn<sup>2+</sup> MnS (buff coloured ppt.) are soluble in dil. HCl, by addition of excess of NaOH gives Mn(OH)<sub>2</sub> ppt. which changes to brown / black by atmospheric O<sub>2</sub>.

$$MnS + 2HCl \longrightarrow MnCl_2 + H_2S$$
(C)

$$MnCl_2 + 2NaOH \longrightarrow Mn(OH)_2 + 2NaCl$$
(C)

$$Mn(OH)_2 + O \longrightarrow MnO_2 + H_2O$$
Air Brown
or black

 $MnO_2$  or  $Mn(OH)_2$  ppt. + conc.  $HNO_3 \longrightarrow ppt.$  dissolves  $MnO_2 + 2HNO_3 \longrightarrow Mn(NO_3)_2 + H_2O + \frac{1}{2}O_2$ 

Divide in two parts:

i. (D) + 
$$H_2O_2$$
 and sodium bismuthate  $\longrightarrow$  purple solution  
 $5NaBiO_3 + 2Mn(NO_3)_2 + 16HNO_3 \longrightarrow$   
 $2HMnO_4 + 5Bi(NO_3)_2 + 5NaNO_3 + 7H_2O$   
Permanganic  
acid (purple)

ii. (D) + PbO<sub>2</sub> 
$$\longrightarrow$$
 Purple solution.

$$2Mn(NO_3)_2 + 5PbO_2 + 6HNO_3 \longrightarrow 2HMnO_4 + 2 H_2O + 5Pb(NO_3)_2$$
Permanganic
acid (purple)

Zn<sup>2+</sup>:

ZnS ppt. (white) are soluble in dil. HCl.

$$ZnS + 2HCI \longrightarrow ZnCl_2 + H_2S$$
(E)

(E) + NaOH -→ white ppt. soluble in excess of NaOH.

$$ZnCl_2 + NaOH \longrightarrow Zn(OH)_2 + NaCl$$
(E) White ppt.

$$Zn(OH)_2 + 2NaOH \longrightarrow Na_2ZnO_2 + 2H_2O$$
  
Sodium zincate

• (E) + Pass  $H_2S \longrightarrow$  White ppt. of ZnS reappears

• 
$$Na_2ZnO_2 + H_2S \longrightarrow 2NaOH + ZnS$$
(D)
Whit

• (E) + CH<sub>3</sub>COOH + K<sub>4</sub>[Fe(CN)<sub>6</sub>]  $\longrightarrow$  bluish white ppt.  $2ZnCl_2 + K_4[Fe(CN)_6] \longrightarrow Zn_2[Fe(CN)_6] \downarrow + 2KCl$ Bluish white ppt.

#### ILLUSTRATION 8.16

(A) (colourless solution) gives white ppt. (B) with NaOH solution but ppt. dissolves in excess of NaOH forming (C). (C) does not give ppt. with  $H_2S$  but on boiling with  $NH_4Cl$ , white ppt. (B) appears. (A) also gives yellow ppt. with  $AgNO_3$ . Identify (A), (B) and (C).

#### ILLUSTRATION 8.17

Test tube (A) contains aqueous zinc acetate solution while test tube (B) contains aq. zinc chloride solution. What happens if  $H_2S$  gas is passed into each solution?

Sol. (A) 
$$Zn (CH_3COO)_2 + H_2S \longrightarrow ZnS + CH_3COOH$$
  
(B)  $ZnCl_2 + H_2S \longrightarrow ZnS + 2HCl$ 

ZnS is precipitated in (A).

In (B) HCl is formed which dissolves ZnS.

#### ILLUSTRATION 8.18

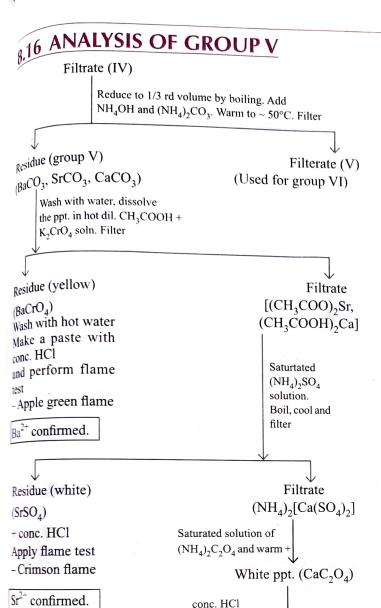
Colourless solution of (A) gives white ppt. (B) with  $AgNO_3$  soluble in aqueous  $NH_3$ . (A) also gives white ppt. (C) with NaOH soluble in excess of it forming (D). (D) gives white ppt. (E) with  $H_2S$ . Identify (A), (B), (C), (D) and (E).

(B): AgCl

(C):  $Zn(OH)_2$ 

(D): NaZnO<sub>2</sub>

(E): ZnS



#### 8.16.1 CHEMICAL REACTIONS INVOLVED

Filtrate of group (V)

i. Filtrate of group (IV)  $\xrightarrow{\text{(i) boil off H}_2S}$  white ppt.

Perform flame test

Crimson red flame

Ca<sup>2+</sup> confirmed.

- ii.  $BaCO_3$ ,  $CaCO_3$ ,  $SrCO_3$ , appears as white ppt.
- iii. Dissolve the white ppt. in  $CH_3COOH$ . Heat

 $MCO_3 + CH_3COOH \xrightarrow{\Delta} (CH_3COOH)_2M + H_2O + CO_2$ 

 $(M = Ba^{2+}, Ca^{2+}, Sr^{2+})$ 

The carbonates dissolve in CH<sub>3</sub>COOH forming acetates.

- iv. (A) +  $K_2CrO_4$   $\longrightarrow$  yellow ppt. (Ba $CrO_4$ )  $(CH_3COOH)_2Ba + K_2CrO_4 \longrightarrow BaCrO_4 \downarrow + 2CH_3COOK$
- v. Flame test: By using a paste of BaCrO<sub>4</sub> with conc. HCl, apple-green flame

Ba2+ confirmed.

- vi. Filtrate (B) obtained after separating BaCrO<sub>4</sub>, may contain (CH<sub>3</sub>COO)<sub>2</sub>Sr, (CH<sub>3</sub>COO)<sub>2</sub>Ca soluble form.
- vii. (B) +  $(NH_4)_2SO_4 \xrightarrow{\Delta}$  white ppt.  $(SrSO_4)$
- viii.  $(CH_3COO)_2Sr + (NH_4)_2SO_4 \longrightarrow SrSO_4 \downarrow + (CH_3COO)NH_4$
- ix. Flame test: By using a paste of SrSO<sub>4</sub> with conc. HCl Crimson flame

Sr<sup>2+</sup> confirmed.

x. Filtrate obtained after separating SrSO<sub>4</sub>, may contain

$$Ca^{2+}$$
 as  $(NH_4)_2[Ca(SO_4)_2]$  (C)

$$(CH_3COO)_2Ca + 2(NH_4)_2SO_4 \longrightarrow (NH_4)_2[Ca(SO_4)_2] + (CH_3COO)NH_4$$

xi. (C) + 
$$(NH_4)_2C_2O_4 \xrightarrow{\text{warm}}$$
 white ppt.  $(CaC_2O_4)$ 

$$(NH_4)_2[Ca(SO_4)_2] + (NH_4)_2C_2O_4 \longrightarrow CaC_2O_4 \downarrow + (NH_4)_2SO_4$$
Ammonium White ppt.

xii. Flame test: By using a paste of CaC<sub>2</sub>O<sub>4</sub> with conc. HCl Crimson red flame

#### ILLUSTRATION 8.19

 $MCl_2 + K_2CrO_4 \longrightarrow yellow ppt.$ 

What can be MCl<sub>2</sub>:

- a. If it is soluble in hot water?
- b. If it gives green colour in flame?

Sol. (A): PbCl<sub>2</sub> (B): BaCl<sub>2</sub>

#### ILLUSTRATION 8.20

(A) (colourless)  $\xrightarrow{\Delta}$  (B) (residue) + (C) (gas) + (D) gas

Solution of (B)  $\xrightarrow{(D)}$  milky

(A) gives brick red colour in flame and decolourises  $MnO_4^{\ominus}/H^{\oplus}$ . Gas (C) burns with blue flame. Identify (A), (B), (C) and (D).

(B): CaO Sol. (A):  $CaC_2O_4$ (C): CO (D): CO,

#### ILLUSTRATION 8.21

CaSO<sub>4</sub> in insoluble but is not precipitated when excess of (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> is added to CaCl<sub>2</sub> explain.

Sol.  $CaSO_4 + (NH_4)_2SO_4 \longrightarrow (NH_4)_2 [Ca(SO_4)_2]$ 

# 8.17 ANALYSIS OF GROUP VI

Centrifugate (V)

Boil off NH<sub>4</sub><sup>⊕</sup> (if present)

Evaporate to dryness extract
with water. Centrifuge

i. Residue (white) (Mg<sup>2+</sup> salts)

> Dissolve in dil. HCl Add NH<sub>4</sub>OH (till alkaline) + Na<sub>2</sub>HPO<sub>4</sub> soln. Shake well and scratch the sides of test tube

White crystalline ppt Mg(NH<sub>4</sub>),PO<sub>4</sub>

Mg<sup>2+</sup> confirmed.

ii. Cobalt-nitrate or (Rinmann's) Charcoal cavity test:

A pink mass is formed.

Mg<sup>2+</sup> confirmed.

Divide in two parts:

i. I Part + CH<sub>3</sub>COOH + sodium cobaltinitrite solution.

Yellow ppt. obtained on standing of K<sub>3</sub>[Co(NO<sub>2</sub>)<sub>6</sub>]

Filterate (A)

(K<sup>⊕</sup> salts)

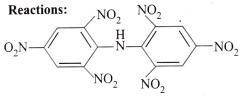
K<sup>⊕</sup> confirmed.

ii. Spot test:

II Part + Dipicrylamine reagent

Orange red-ppt. uneffected by few drops of dil. HCl.

 $K^{\oplus}$  confirmed.



Note: Dipicrylamine reagent (Hexa-nitro-diphenylamine) is prepared by dissolving 0.2g of dipcrylamine in 20 mL of 0.1 N Na<sub>2</sub>CO<sub>3</sub> and filtering the cooled liquid.

Note: H atom of NH group is replaceable by metals.

NH<sub>4</sub> must be absent

Mg<sup>2+</sup> does not interfere.

iii. Flame test: A crimson colour using cobalt blue glass.

 $K^{\oplus}$  confirmed.

#### 8.17.1 CHEMICAL REACTIONS INVOLVED

For Mg<sup>2+</sup> ion:

Filtrate of group V + NH<sub>4</sub>OH +Na<sub>2</sub>HPO<sub>4</sub>  $\longrightarrow$  fine Crystalline ppt. on scratching the side of the test tube MgCl<sub>2</sub> + NH<sub>4</sub>OH + Na<sub>2</sub>HPO<sub>4</sub>  $\longrightarrow$  Mg(NH<sub>4</sub>)PO<sub>4</sub>  $\downarrow$  + 2NaCl + H<sub>2</sub>O White ppt. For K<sup>⊕</sup> ion:

Filtrate (A) + CH<sub>3</sub>COOH + Sodium cobaltinitrite solution (in excess)

→ yellow ppt. on standing

 $Na_{3}[Co(NO_{2})_{6} + 3KCI \longrightarrow K_{3}[Co(NO_{2})_{6}] \downarrow + 3NaCI$ (excess)
White ppt. (Potassium cobaltinitrite)

Potassium cobltinitrite is insoluble in  $CH_3COOH$ .  $(NH_4^{\oplus})$  salts give a similar test with sodium cobaltinitrite and therefore must be completely eliminated before doing the test for  $K^{\oplus}$  ions.

#### ILLUSTRATION 8.22

(A) (orange) 
$$\xrightarrow{\Delta}$$
 gas (B) + residue (C) (green) + H<sub>2</sub>O  
NaOH  
 $\Delta$ 

Gas (D)  $\xrightarrow{\text{HCl}}$  white fumes

Gas (B) 
$$\xrightarrow{Al}$$
 (E)  $\xrightarrow{H_2O}$  gas (B)  
Residue (C)  $\xrightarrow{\text{conc. HCl}}$  (F)  $\xrightarrow{\text{NaOH, H}_2O_2}$  (G) (yellow)  $\xrightarrow{\text{CH}_3\text{COOH}}$  (CH<sub>3</sub>COO)<sub>2</sub>Pb yellow (H)

Identify (A) to (H) and explain reactions.

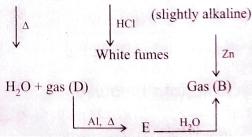
**Sol.** (A): 
$$(NH_4)_2Cr_2O_7$$
 (B):  $N_2$  (C):  $Cr_2O_3$ 

(D): 
$$NH_3$$
 (E): AIN

#### ILLUSTRATION 8.23

Identify (A), (B), (C), (D) and (E).

(A) NaOH  $\xrightarrow{\Delta}$  gas (B) + aq. solution (C)



Sol. (A): 
$$NH_4NO_2$$
 (B):  $NH_3$  (C):  $NaNO_2$  (D):  $N_2$  (E): AIN

# $\frac{8.18 \text{ ANALYSIS OF ZERO}}{\text{GROUP } (\text{NH}_{4}^{\oplus})}$

S.No.	Experiment	Observation	Inference
1. i.	Mixture + 1–2 mL of NaOH soln. Heat	Smell of NH <sub>3</sub> observed	NH <sub>4</sub> <sup>⊕</sup> may
ii.	Bring a glass rod dipped in conc. HCl at the mouth of test tube	White dense fumes (NH <sub>4</sub> Cl) are observed	

2. ii t t 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1	n above test hrough Nessler's reagent or Water extract of the nixture + NaOH soln. + Nessler's	Brown colour ppt. is obtained	NH <sub>4</sub> <sup>⊕</sup> confirmed
1	reagent		

# 18.1 CHEMICAL REACTIONS INVOLVED

1. i. 
$$NH_4Cl + NaOH \longrightarrow NaCl + NH_4OH$$
  
 $NH_4OH \longrightarrow NH_3 \uparrow + H_2O$ 

ii. 
$$NH_3 + HCl \longrightarrow NH_4Cl$$

$$1. NH4OH + 2K2HgI4 + 3NaOH \longrightarrow \left[O \underset{Hg}{\longleftarrow} NH2\right]I$$

$$+ 4KI + 3NaI + 3H2O$$

#### LUSTRATION B.24

Colourless salt (A) gives apple-green flame with conc. HCl. (A) m reaction with dil. H<sub>2</sub>SO<sub>4</sub> gives light brown fumes (D) turning Kl-starch paper blue.

(A) + CH<sub>3</sub>COOH + 
$$K_2$$
CrO<sub>4</sub>  $\longrightarrow$  yellow ppt. (B)

$$(A) + H_2SO_A \longrightarrow (C)$$
 (white ppt.) + (D)

$$(D) + CH_2NH_2 + CH_3OH + H_2O + gas (E)$$

$$(E) + Mg \xrightarrow{\Delta} (F)$$

$$(F) + H_2O \longrightarrow NH_3$$

Identify (A) to (F) and explain reactions.

- (A):  $Ba(NO_2)_2$  (B):  $BaCrO_4$  (C):  $BaSO_4$

- (D):  $HNO_2$
- (E): N<sub>2</sub>
- (F):  $Mg_3N_2$

# CONCEPT APPLICATION EXERCISE 8.1

- 1. Identify (A) to (H).
  - Mineral (A)  $\xrightarrow{\text{dil. H}_2\text{SO}_4}$  (B) + (C) + (D) (gas)
  - (D) +  $(CH_3COO)_2Pb \xrightarrow{\Delta} black ppt.$
  - $(B) + (C) \xrightarrow{(D)} E (black ppt.)$

separated from (C) by filtration

- (E) +  $HNO_3 \xrightarrow{\Delta}$  (F) (blue coloured solution)
- $(F) + K_4[Fe(CN)_6] \longrightarrow chocolate coloured ppt.$
- $(C) + K_3[Fe(CN)_6] \longrightarrow blue(H)$
- 2. An aqueous solution of salt (A) gives a white crystalline precipitate (B) with NaC1 solution. The filtrate gives

- a black precipitate (C) when H<sub>2</sub>S is passed through it. Compound (B) dissolves in hot water and the solution gives yellow precipitate (D) on treatment with potassium iodide and on cooling. The compound (A) does not give any gas with dilute HC1 but liberates a reddish brown gas on heating. Identify the compounds (A) to (D) giving the involved equations.
- 3. A white amorphous powder (A) when heated gives a colourless gas (B), which turns lime water milky and the residue (C) which is yellow when hot but white when cold. The residue (C) dissolves in dilute HC1 and the resulting solution gives a white precipitate on addition of potassium ferrocyanide solution. (A) dissolves in dilute HC1 with the evolution of a gas which is identical in all respects with (B). The solution of (A) as obtained above gives a white precipitate (D) on addition of excess of NH,OH and on passing H2S. Another portion of this solution gives initially a white precipitate (E) on addition of NaOH which dissolves in excess of it. Identify (A) to (E).
- 4. Compound (A) is a light green crystalline solid. It gives the following tests:
  - It dissolves in dilute sulphuric acid. No gas is produced.
  - ii. A drop of KMnO<sub>4</sub> is added to the above solution. The pink colour disappears.
  - iii. Compound (A) is heated strongly. Gases (B) and (C) with pungent smell came out. A brown residue (D) is left behind.
  - iv. The gas mixture [(B) and (C)] is passed into a dichromate solution. The solution turns green.
  - v. The green solution from step (iv) gives a white precipitate (E) with a solution of barium nitrate.
  - vi. Residue (D) from (v) is heated on charcoal in reducing flame, it gives a magnetic substance.

Identify the compounds (A) to (E).

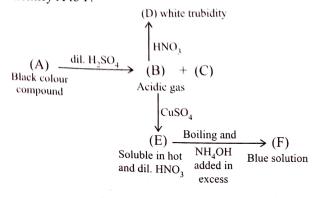
5. Identify A to F.

(F) 
$$\leftarrow \frac{K_4[Fe(CN)_6]}{(Blue solution)}$$
 (A)  $\xrightarrow{BaCl_2}$  (B) + (C)

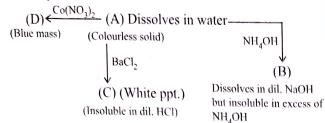
(Blue solution) White ppt.

(B)  $\leftarrow (B)$  (B)

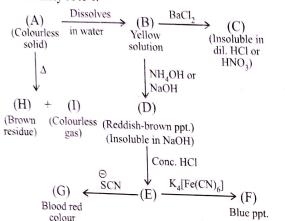
**6.** Identify A to F.



#### 7. Identify A to D.

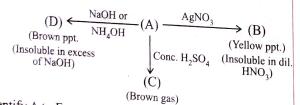


#### **8.** Identify A to I.

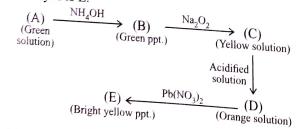


#### 9. Identify A to G.

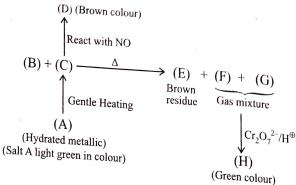
#### 10. Identify A to D.



#### 11. Identify A to E.



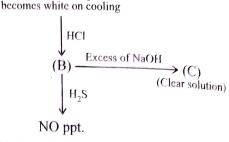
#### 12. Identify A to H.



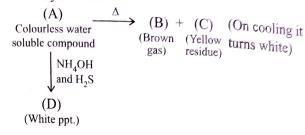
#### 13. Identify A to C.

(A) (white ppt.)

water insoluble solid turns yellow on heating and



#### 14. Identify A to D.



#### ANSWERS

<b>1.</b> (A): CuFeS <sub>2</sub>	(B): CuSO <sub>4</sub>	(C): FeSO	
(D): H <sub>-</sub> S	(E). Cc	(=).10004	

(D): 
$$H_2S$$
 (E):  $CuS$  (F):  $Cu(NO_3)_2$ 

(G): 
$$\operatorname{Cu}_2[\operatorname{Fe}(\operatorname{CN})_6]$$

(C): 
$$ZnCO_3$$
 (B):  $CO_2$  (C):  $ZnO$  (D):  $ZnS$ 

(C): 
$$Z_{nO}$$
 (D):  $Z_{nS}$ 

(E): 
$$Zn(OH)_2$$

(D): 
$$Fe_2O_3$$
 (E):  $BaSO_4$ 

(D): 
$$(Cu_2I_2 + I_3^{\Theta})$$
 (E):  $(Cu_2I_2 + I^{\Theta} + S_4O_6^{2-})$ 

(F): 
$$Cu_2[Fe(CN)_6]$$

7. (A): 
$$Al_2(SO_4)_3$$
 (B):  $Al(OH)_3$  (C):  $BaSO_4$ 

8. (A): 
$$Fe_2(SO_4)_3$$

(C): 
$$\operatorname{BaSO}_4$$
 (B):  $\operatorname{Fe}_2(\operatorname{SO}_4)_3$  solution (D):  $\operatorname{Fe}(\operatorname{OH})$ 

(E): 
$$FeCl_3$$
  
(G):  $Fe(SCN)_3$   
(F):  $Fe_4[Fe(CN)_6]_3$   
(H):  $Fe_5O_5$ 

9. (A): 
$$FeSO_4$$
 (B):  $BaSO_4$  (C):  $Fe_2$ 

(D): 
$$SO_2$$
 (E):  $SO_3$  (C):  $Fe_2O_3$  (F):  $FeCl_3$ 

(C): Na<sub>2</sub>CrO<sub>4</sub>

(A). 
$$CrCl_3$$
 (B):  $Cr(OH)_3$  (C):  $PbCrO_4$ 

12. (A): FeSO<sub>4</sub>·7H<sub>2</sub>O (B): FeSO<sub>4</sub> (C): 7H<sub>2</sub>O (D): Fe[(H<sub>2</sub>O)<sub>5</sub>NO]SO<sub>4</sub> (E): Fe<sub>2</sub>O<sub>3</sub> (F): SO<sub>2</sub> (G): SO, (H): Cr<sup>3+</sup>solution 13. (A): ZnO (B): ZnCl, (C): Na<sub>2</sub>ZnO<sub>2</sub> 14. (A): Zn(NO<sub>3</sub>)<sub>2</sub> (B): NO, (C): ZnO (D): ZnS

# Viva-Voce Questions and Answers

## <sub>pART-A</sub> (Analysis of Anions)

#### 1. What is a group reagent?

- ins. The reagent which is employed in identifying a group of radicals is known as a group reagent.
- 2. Why sodium carbonate extract is used for testing acid radicals?
- ans. The scheme followed for the systematic analysis of acid radicals is based on sodium salts of acid radicals. Other basic radicals if present may interfere with their salts.
- 3. Can we use sodium bicarbonate in place of sodium carbonate in preparing an extract for detection of anions?
- Ans. No. Metal bicarbonates formed by double decomposition will remain in solution.
- 4. Why is sodium carbonate extract acidified before performing the confirmatory tests for anions?
- Ans. Sodium carbonate extract in addition to the sodium salts of anions contain carbonate also. On heating with the test reagent carbonates of certain metals precipitate which interere in the detection of acid redicals. Because of this,  $Na_2CO_3$  is decomosed by adding HCl, HNO3,  $H_2SO_4$ , depending upon the nature of test.
- 5. Can sodium carbonate extract be used test for  $CO_3^{2-}$ ions?
- Ans. No, because it already contains these ions.
- 6. What is lime water?
- Ans. It is a water solution of calcium hydroxide.
  - 7. Why does lime water turns milky on bubbling  $\mathrm{CO}_2$  gas through it?
- Ans. Initially CaCO<sub>3</sub> (causing milkiness) is formed which disappears due to the formation of  $Ca(HCO_3)_2$  which  $CO_2(g)$ is passed for long time.
- 8. Name the anions which give brown fumes on reacting with dilute / conc. H<sub>2</sub>SO<sub>4</sub>.
- Ans. With dilute  $H_2SO_4$ ,  $NO_2^{\odot}$  ion gives brown fumes. With conc.  $H_2SO_4$  both  $Br^{\Theta}$  and  $NO_3^{\Theta}$  ions give brown fumes.
- 9. Why does a paper soaked in K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> solution turn greeen in the detection of SO<sub>3</sub><sup>2-</sup>ion?
- Ans. The paper turns green because the SO<sub>2</sub> gas evolved from  $SO_3^{2-}$  salt reduces  $K_2Cr_2O_7$  to  $Cr_2(SO_4)_3$  which turns the paper green.

- 10. Can filter paper dipped in silver nitrate solution instead of lead acetate paper be used for testing a sulphide?
- Ans. Yes, a paper dipped in AgNO<sub>3</sub> when exposed to the vapours of H<sub>2</sub>S turns black due to the formation of silver sulphide.  $2AgNO_3 + H_2S \longrightarrow Ag_2S + 2HNO_3$ 
  - 11. A gas evolved with effervescence on treating a salt with dil. HCl may be CO2 or SO3. How will you distinguish between them?
- Ans. a. SO<sub>2</sub> has a pungent burning sulphur smell, whereas CO<sub>2</sub> is odourless.
  - b. SO<sub>2</sub> turns potassium dichromate paper green, whereas CO<sub>2</sub> does not.
  - 12. How will you distinguish between carbonate and bicarbonate ions?
- Ans. MgSO<sub>4</sub> gives a white ppt. with carbonate ions in cold solution while a white ppt. is obtained with bicarbonate ions in hot solution only.

Phenolphthalein gives a pink colour with carbonate ions and no colour is obtained with bicarbonate ions.

- 13. How can sulphide ions be distinguished from sulphite ions?
- Ans. AgNO<sub>3</sub> forms white ppt. with sulphite ions while a black precipitate is obtained with sulphide ions.

BaCl, gives white ppt. with sulphite ions while no ppt. is obtained with sulphide ions.

FeCl<sub>3</sub> solution gives a red colouration with sulphite ions and a black ppt. is formed with sulphide ions.

- 14. How will you distinguish between sulphate and thiosulphate ions?
- Ans. AgNO<sub>3</sub> gives white ppt. with thiosulphate ions which turns black on standing whereas no ppt. is obtained with sulphate

FeCl<sub>3</sub> gives purple colour with thiosulphate ions which disappears gradually and no ppt. or colouration is obtained in case of sulphate.

- 15. How will you distinguish between sulphite and sulphate
- Ans. BaCl, gives a white ppt. with both sulphite and sulphate

BaSO<sub>3</sub> is soluble in conc. HCl whereas BaSO<sub>4</sub> is insoluble in conc. HCl.

FeCl<sub>3</sub> solution gives a red colour with sulphite and no colour is obtained with sulphate.

- 16. How can nitrite ion be distinguished from nitrate ion?
- Ans. Nitrate ion gives a brown ring with FeSO<sub>4</sub> and conc. sulphuric acid. But with nitrite ion a black coloured solution is obtained.
  - 17. What is the formula of compound present in brown ring?
- **Ans.**  $3Fe^{2+} + NO_3^{\ominus} + 4H^{\oplus} \longrightarrow 3Fe^{3+} + NO + 2H_2O$  $FeSO_4 + NO \longrightarrow FeSO_4$ .NO or  $[Fe(H_2O)_5NO]SO_4$ 
  - 18. Why is a freshly prepared solution of  ${\rm FeSO_4}$  used for the detection of nitrate and nitrite?



- **Ans.** This is because Fe<sup>2+</sup> ions on long standing are oxidised to Fe<sup>3+</sup> ions which are not used for the detection of nitrate or nitrite.
  - 19. Why does only the organic layer assure colour and not the aqueous layer when the tests for halides are done?
- **Ans.** Both Br<sub>2</sub> and I<sub>2</sub> are covalent. They have preference for organic layer.
  - 20. What happens when chloride, bromide and iodide are separately heated with conc. H<sub>2</sub>SO<sub>4</sub>?
- **Ans. a.** Chloride gives HCl gas which gives thick white fumes with aqueous ammonia.
  - **b.** Bromide gives reddish-brown Br<sub>2</sub> vapours.
  - **c.** Iodide gives violet vapours of iodine which turns starch paper blue.
  - 21. How do you distinguish between Br and NO ions?
- **Ans.** Treat the salt with conc.  $H_2SO_4$ . Pass the reddish-brown gas evolved through  $FeSO_4$  solution. If it turns black, it is  $NO_3^{\ominus}$ . In case it does not turn black, the anion is  $Br^{\ominus}$ .
  - 22. Given salt is a bromide or iodide. How will you identify it by treating the salt with chlorine water and CS<sub>2</sub>?
- **Ans.** If  $CS_2$  layer assumes an orange colour, it is  $Br^{\Theta}$ . If  $CS_2$  layer assumes a violet colour, it is  $I^{\Theta}$ .
  - 23. Why does the chromyl chloride test fail with  $Br^{\ominus}$  and  $I^{\ominus}?$
- **Ans.** Because both chromyl bromide and chromyl iodide are not volatile in nature.
- 24. For testing SO<sub>4</sub><sup>2-</sup> with BaCl<sub>2</sub> solution, why should sodium carbonate not be acidified with too much of conc. HCl.
- Ans. In the presence of conc. HCl, BaCl<sub>2</sub> itself will be precipitated. The precipitated BaCl<sub>2</sub> is mistaken as BaSO<sub>4</sub>.
- 25. Can any other reagent in place of lime water be employed for identification of CO<sub>2</sub> gas?
- **Ans.** Yes, M(OH) can be employed.
  - 26. At times the solution of lime water appears milky. Comment.
- Ans. The lime water lying in the reagent bottle absorbs  $CO_2$  gas from the atmosphere and produces white insoluble  $CaCO_3$ .  $Ca(OH)_2 + CO_2 \longrightarrow CaCO_3(s) + H_2O$
- 27. Name the gas other than CO<sub>2</sub> which also turns lime water milky.
- Ans.  $SO_2$  gas also turns lime water milky as insoluble  $CaSO_3$  is produced.
- 28. Why is it necessary to test for the acid radicals first (with dilute) H<sub>2</sub>SO<sub>4</sub> and then with conc. H<sub>2</sub>SO<sub>4</sub>?
- **Ans.** There are some ions like,  $SO_3^{2-}$ ,  $S^{2-}$ ,  $NO_2^{\Theta}$ , and  $CH_3COO^{\Theta}$  which can react with dilute/conc.  $H_2SO_4$  whereas ions like  $CI^{\Theta}$ ,  $Br^{\Theta}$ ,  $I^{\Theta}$ ,  $NO_3^{\Theta}$ , etc. react only with conc.  $H_2SO_4$ .

Now if conc.  $H_2SO_4$  is used first then the anions of both the types will react. Hence, it is desired to test acid radicals first with dilute  $H_2SO_4$  and then with conc.  $H_2SO_4$ .

- 29. What is chromyl chloride test? Why is it so named?
- Ans. Chlorides of metals other than heavy ones, e.g.  $Hg^{2+}$ , on reacting with conc.  $H_2SO_4$  and  $K_2Cr_2O_7$  produce orange colour vapours, which on reacting with NaOH and lead acetate produce yellow ppt. of PbCrO<sub>4</sub>.
  - Orange colour vapours are that of chromyl chloride,  $CrO_2Cl_2$ , hence the test is so named.
- 30. Sodium carbonate extract is acidified with HNO<sub>3</sub> only in the identification of halides. Comment.
- Ans. HCl and H<sub>2</sub>SO<sub>4</sub> are not used, as the acids react with the test reagent AgNO<sub>3</sub> and form ppt. of AgCl and Ag<sub>2</sub>SO<sub>4</sub> respectively. Because of this only HNO<sub>3</sub> is used for the purpose.

#### **PART-B (Dry Tests)**

- 31. Why do salts of the following ions  $Cu^{2^+}$ ,  $Ba^{2^+}$ ,  $Sr^{2^+}$ ,  $Ca^{2^+}$ ,  $Na^{\oplus}$  and  $K^{\oplus}$  impart colour to the flame?
- Ans. This is due to the fact that the chlorides of these are volatile and at higher temperature they ionise giving respective cations. Since the energy of bunsen flame is constant, different elements are excited to different levels due to difference in their ionisation energies. When these excited electrons return to their original energy level, they emit the same amount of energy absorbed during excitation in the form of electromagnetic radiation which appears in the visible region of the spectrum, thereby imparting a characteristic colour to flame.
  - 32. Why is HCl employed in flame test?
- Ans. Only the volatile compounds of cations impart colour to the flame. Only metal chlorides are volatile whereas their sulphates, nitrates etc. are not. Thus, HCl is used to convert cations into their volatile chlorides.
  - 33. What type of flame is employed to perform the flame test? How is it obtained?
- **Ans.** A non-luminous flame is employed to perform the test. It is obtained by keeping the holes of the burner open.
  - 34. Why is a green flame not obtained in the case of barium sulphate or phosphate?
- Ans. Both barium sulphate and phosphate are insoluble and cannot be easily converted into chlorides. Therefore, the green flame is either indistinct or visible with difficulty.
  - 35. Can we perform the charcoal cavity test without the addition of fusion mixture (Na<sub>2</sub>CO<sub>3</sub> and K<sub>2</sub>CO<sub>3</sub>) with the carbonate of metals?
- Ans. Yes, we can directly perform the charcoal cavity test without the addition of fusion mixture because the latter simply converts the substances into carbonates in fused state. Carbonates of metals on heating in the charcoal cavity are reduced to metallic state.

Why do we not perform borax bead test with the white

This test is applied for the identification of the cations of the coloured salt only because the of the coloured salt only because the borax forms the corresponding metaborates which possess characteristic colour. For example, with CuSO<sub>4</sub>, the reaction is

$$CuSO_4 + B_2O_3 \longrightarrow Cu(BO_2)_2 + SO_3$$
(from borax) (blue)

#### What is the composition of the bead obtained when borax is heated in the flame?

It consists of a mixture of sodium metaborate and boric anhydride.

#### 18. Why is a small quantity of mixture used in the borax beat test?

108 avoid the formation of dark and opaque bead which in subsequent treatment cannot be recognised easily.

#### 10. Name the cations which can be identified by flame test.

n, 
$$Ba^{2+}$$
 - Apple green  $Sr^{2+}$  - Crimson

$$Sr^{2+}$$
 – (

#### PART-C (Analysis of Cations)

#### 40. Why is it necessary to prepare original solution for the detection of basic radicals?

Ans. The detection of basic radicals depends on the behaviour of ions in solution. For this purpose the preparation of original solution is necessary as it furnishes free ions in solution.

## 41. Why do we not prefer to prepare original solution in conc. H<sub>2</sub>SO<sub>4</sub> or conc. HNO<sub>3</sub>?

Ans. It is not advisable to prepare original solution in conc.  $HNO_3$ or conc. H<sub>2</sub>SO<sub>4</sub> because these are oxidising agents and they oxidise H<sub>2</sub>S in group II to produce a yellow ppt. of sulphur.

$$H_2SO_4 \longrightarrow H_2O + SO_2 + [O]$$

$$HNO_3 \longrightarrow H_2O + NO_2 + [O]$$

$$H_2S + O \longrightarrow H_2 + S(s)$$

Also Pb<sup>2+</sup>, Ba<sup>2+</sup>, Sr<sup>2+</sup>, Ca<sup>2+</sup> are precipitated as their insoluble sulphates in presence of conc.  $H_2SO_4$ .

BaCl<sub>2</sub> + H<sub>2</sub>SO<sub>4</sub> 
$$\longrightarrow$$
 BaSO<sub>4</sub>(s) + 2HCl

# 42. What is solubility product? Explain its importance in qualitative analysis.

Ans. The ionic product in a saturated solution of an electrolyte at a given temperature is always a constant quantity and is termed as solubility product. Whenever in a solution the ionic product exceeds the solubility product, the precipitation occurs due to the supersaturation of solution.

43. What is the basis of classification of cations into different

Ans. The different cations are classified under six groups depending upon the difference in the solubilities of their chlorides, sulphide hydroxides and carbonates at different pH values.

# 44. Why are only $Pb^{2+}, Ag^{\oplus}$ and $Hg_2^{\ 2^+}$ ions precipitated in

**Ans.** Out of all the chlorides, those of  $Pb^{2+}$ ,  $Ag^{\oplus}$  and  $Hg_2^{2+}$  are insoluble. HCl is the reagent of group I. Thus, chlorides of  $Pb^{2+}$ ,  $Ag^{\oplus}$  and  $Hg_2^{2+}$  are precipitated in group I.

$$AgNO_3 + HCl \longrightarrow AgCl(s) + HNO_3$$

(White ppt.)

Other cations remain in solution because their chlorides are soluble.

#### 45. Why is lead placed in group I as well as in II?

Ans. This is due to fact that lead is not completely precipitated in group I as lead chloride. PbCl<sub>2</sub> is also soluble in hot water. Therefore, the lead which escapes precipitation in group I as PbCl<sub>2</sub> is precipitated in the group II as PbS.

#### 46. Is it necessary to acidify a solution before group II cations are precipitated with H<sub>2</sub>S?

Ans. Yes, because for the precipitation of cations of group II only small concentration of sulphide ions (S<sup>2-</sup>) is required. This condition is achieved by passing H2S gas in a solution acidified with HCl (dil.). Due to common ion effect, concentration of S2- ions decreases as presence of hydrochloric acid suppresses the ionisation of H<sub>2</sub>S, resulting only in the precipitation of sulphides of group II metals. Other metal sulphides remain in solution as they require

higher concentration of S<sup>2-</sup> ions for their precipitation. 47. Give the reason for the formation of a light yellow or white ppt. in the group II even if it may not be because of some metal ion.

Ans. Yellow or white ppt. is formed due to the oxidation of H<sub>2</sub>S gas by some oxidising agents to sulphur which floats on the surface.

$$BaSO_3 + 2HCl + 2H_2S \longrightarrow BaCl_2 + 3H_2O + 3S$$

$$2NaNO_2 + H_2S + 2HCl \longrightarrow 2NO + 2NaCl + 2H_2O + S$$

(yellow)

$$2 \operatorname{FeCl}_3 + \operatorname{H}_2 S \longrightarrow 2 \operatorname{FeCl}_2 + 2 \operatorname{HCl} + S$$

#### 48. Why do we prefer HCl for preparing solutions of cations?

Ans. Because most of the salts are soluble in HCI except those of group I.

49. Is it advisable to use conc. HCl in place of dilute HCl for preparing original solution.

Ans. Conc. HCl can be used but to ensure the precipitation of Pb<sup>2+</sup> as PbCl<sub>2</sub>, the solution is prepared in dil. HCl as PbCl<sub>2</sub> dissolves in conc. HCl due to complex formation.

50. Why is it essential to boil off H<sub>2</sub>S gas before proceeding to group III.

- **Ans.** Otherwise the sulphides of group IV will also be precipitated along with precipitate of group III.
  - 51. Can the solution be acidified with HNO<sub>3</sub> in group II before passing H<sub>2</sub>S gas?
- **Ans.** No, HNO<sub>3</sub> being oxidising in nature oxidises H<sub>2</sub>S gas to form colloidal sulphur which makes the analysis complicated.
  - 52. What can it be, if the precipitate of group I is soluble in hot water and insoluble in cold water?

Ans. PbCl,

- 53. Why is H<sub>2</sub>SO<sub>4</sub> never employed for preparing original solution for the identification of cations?
- Ans. Ba<sup>2+</sup>, Sr<sup>2+</sup> and Pb<sup>2+</sup> are precipitated as insoluble sulphates.
- 54. Group I filtrate is made moderately acidic before proceeding to group II. Explain.
- Ans. Precipitation of the sulphide can occur only when the ionic product  $[M^{2+}]$   $[S^{2-}]$  exceeds the solubility product of the sulphide, MS.

In the presence of acid, the ionisation of  $H_2S$  is suppressed due to the increased concentration of  $H^{\oplus}$ . As a result, there are only few  $S^{2-}$  ions in solution which are enough to precipitate only group II cations as sulphides, e.g. CuS, PbS, etc.

But for the precipitation of CdS, the concentration of  $S^{2-}$  is not enough. Hence the concentration of  $(H^{\oplus})$  should be further decreased by diluting the solution so that the  $H_2S$  is ionised extensively. As a result  $S^{2-}$  ions are made available in sufficient quantity which can precipitate the  $Cd^{2+}$  ions. i.e. ionic product  $[Cd^{2+}][S^{2-}]$  exceeds solubility product of CdS.

- 55. What is the use of adding nitric acid in the precipitation of group III cations as hydroxides.
- Ans. Nitric acid is useful in the oxidation of ferrous salts to ferric salts in group III.

 $3FeSO_4 + 4HNO_3 \longrightarrow Fe_2(SO_4)_3 + Fe(NO_3)_3 + NO + 2H_2O$ 

- 56. Why do we add excess of NH<sub>4</sub>Cl and NH<sub>4</sub>OH in the precipitation of group III cations?
- **Ans.** The solubility product of hydroxides of cations of group III is extremely low.

 $\mathrm{NH_4Cl}$  suppressess the ionisation of  $\mathrm{NH_4OH}$  to a great extent due to common ion effect. As a result, low concentration of  $\mathrm{OH}^{\circleddash}$  is made available for precipitating group III cation hydroxides.

Other hydroxides remain in solution as they require higher concentration of OH<sup>©</sup> ions for precipitation as hydroxides.

- 57. Why is it essential to oxidise ferrous salt to ferric salt in group III?
- Ans. This is because the ferrous salts are not completely precipitated as Fe(OH)<sub>2</sub> in the presence of NH<sub>4</sub>Cl on the addition of NH<sub>4</sub>OH and thus iron will also be precipitated in the group IV as FeS on passing H<sub>2</sub>S.

Therefore, to precipitate iron completely in the group III, it is necessary to oxidise ferrous salt to ferric salt.

- 58. Can NH<sub>4</sub>Cl be replaced by any other ammonium salt for the precipitation of group III cations?
- Ans. Yes, NH<sub>4</sub>NO<sub>2</sub> can be used in place of NH<sub>4</sub>Cl for the precipitation of group III cations. Ammonium sulphate cannot be used as it may precipitate Ca<sup>2+</sup>, Ba<sup>2+</sup> and Sr<sup>2+</sup> as insoluble sulphates.
  - 59. How will you distinguish between ferrous and ferric salts?
- Ans. Ammonium sulphocyanide does not give any colouration with ferrous salt while it gives a blood-red colour with ferric salt.

Potassium ferricyanide produces a blue ppt. with ferrous salt while a red colouration is obtained with ferric salt.

- 60. Can we add NH<sub>4</sub>OH first and NH<sub>4</sub>Cl later in the analysis of group III cations?
- Ans. No, the function of NH<sub>4</sub>Cl is to suppress ionisation of NH<sub>4</sub>OH and thereby it prevents precipitation of Zn(OH)<sub>2</sub>, Mg(OH)<sub>2</sub>, Mn(OH)<sub>2</sub>, etc.

  In case NH<sub>4</sub>OH is added first these hydroxides will be immediately precipitated. Addition of NH<sub>4</sub>Cl afterwards will be of no use.
- 61. Can we use NaCl and NaOH in place of NH<sub>4</sub>Cl and NH<sub>4</sub>OH in the group III cation precipitation.
- Ans. No, NaOH is a strong base and highly ionised. Even in the presence of NaCl,  $[OH^{\Theta}]$  will be large enough to precipitate  $Zn(OH)_2$ ,  $Mg(OH)_2$ , etc.
  - 62. Why are Zn, Mn, Ni, Co not precipitated in the group III as hydroxides?
- Ans. The solubility products of hydroxides of Zn, Mn, Ni and Co are very high. For this purpose they require high concentration of OH<sup>⊕</sup> ions. This is not possible in the group III as NH<sub>4</sub>Cl suppresses the ionisation of NH<sub>4</sub>OH due to common ion effect.
- 63. Why are the group IV cations not precipitated as sulphides on passing H<sub>2</sub>S gas through group II solution?
- Ans. For the precipitation of cations of group IV, a very large concentration of sulphide ions (S<sup>2-</sup>) is required which is not available in the group II as the ionisation of H<sub>2</sub>S is suppressed by HCl (common ion effect).

In precipitating the cations of group IV, high concentration of  $S^{2-}$  ions is required as  $OH^{\odot}$  ions released by  $NH_4OH$  unite with  $H^{\oplus}$  ions given by  $H_2S$ . Thus the solubility product is exceeded and the cations of group IV are precipitated as ZnS, NiS, MnS and CoS.

- 64. Why is a brownish ppt. obtained in group III even if iron, aluminium and chromium are absent?
- **Ans.** When NH<sub>4</sub>Cl is not present in sufficient amount, Mn is precipitated as MnO<sub>2</sub>·H<sub>2</sub>O which is brown in colour.
  - 65. Why sometimes, a black coloured precipitate obtained in group IV even if nickel and cobalt ions are absent?

A black coloured precipitate is obtained in the group IV due to the incomplete removal of iron in group III. Iron escapes precipitation in group III due to lack of enough NH<sub>4</sub>OH. Fe<sup>+3</sup> is reduced to Fe<sup>2+</sup> by H<sub>2</sub>S which finally gets precipitated as FeS (black) in group IV even when both Co and Ni are absent.

$$FeCl_2 + H_2S \longrightarrow 2HCl + FeS(s)$$
(Black ppt.)

# 66. Why excess of NH<sub>4</sub>OH is used in precipitating the sulphides of group IV cations?

The solubility product of group 1V radicals is greater than that of group II ions. Therefore, a higher concentration of S<sup>2-</sup> ions is required to precipitate group IV ions as their sulphides. Now to get a higher concentration of S<sup>2-</sup> ions, H<sub>2</sub>S gas is passed in presence of NH<sub>4</sub>OH. The OH ions from NH<sub>4</sub>OH neutralise the H<sup>®</sup> ions from H<sub>2</sub>S to form undissociated water molecules. The removal of H<sup>®</sup> ion causes more H<sub>2</sub>S to dissociate or ionise, thus increasing the concentration of S<sup>2-</sup> ions and so the product [M<sup>2+</sup>] [S<sup>2-</sup>] exceeds the solubility products of the sulphides of Zn, Mn, Ni and Co and hence they are precipitated.

$$(M = Zn, Mn, Co \text{ or Ni})$$
  
 $2NH_4OH \Longrightarrow 2NH_4^{\oplus} + 2OH^{\ominus}$   
 $H_2S \Longrightarrow 2H^{\oplus} + S^{2-}$   
 $2H^{\oplus} + 2OH^{\ominus} \Longrightarrow 2H_2O$ 

# 67. Why sometimes colloidal precipitate is obtained in group IV? Comment.

Ans. To prevent the colloidal precipitate, ammonium chloride must be present in large amount. H<sub>2</sub>S should not be passed for long.

# 68. Why is NH<sub>4</sub>Cl essential in the precipitation of group V cations?

Ans. Ammonium chloride prevents the precipitation of  ${\rm Mg}^{2^+}$  as  ${\rm MgCO}_3$  by the group reagent  ${\rm (NH_4)}_2{\rm CO}_3$  by lowering down its dissociation into  ${\rm NH_4}^\oplus$  and  ${\rm CO_3}^{2^-}$  ions.

# 69. Does the excess of $NH_4Cl$ affect the precipitation of group V cations by $(NH_4)_2CO_3$ ?

Ans. Yes, the concentration of  $CO_3^{2-}$  is decreased because the common ion  $NH_4^{\oplus}$  suppresses the ionisation of  $(NH_4)_2CO_3$ .

# 70. Why are all aqueous solutions of the cobaltous salts pink?

Ans. All aqueous solutions of cobaltous salts are pink due to the formation of  $[Co(H_2O)_6]^{2+}$  ions.

# 71. At times NH<sub>4</sub>OH is added before adding (NH<sub>4</sub>)<sub>2</sub>CO<sub>3</sub> to precipitate group V cations. Explain.

Ans. Ammonium hydroxide reacts with bicarbonate present as impurity in  $(NH_4)_2CO_3$  as follows:

NH<sub>4</sub>HCO<sub>3</sub> + NH<sub>4</sub>OH 
$$\longrightarrow$$
 (NH<sub>4</sub>)<sub>2</sub>CO<sub>3</sub> + H<sub>2</sub>O

The presence of bicarbonate is undesirable as the bicarbonates of Ba, Sr and Ca are soluble in water.

# 72. How will you remove the excess of NH<sub>4</sub>Cl before adding (NH<sub>4</sub>)<sub>2</sub>CO<sub>3</sub> for the precipitation of group V?

Ans. NH<sub>4</sub>Cl is removed by treating the filtrate from group IV with conc. HNO<sub>3</sub>. On heating to dryness, ammonium chloride is decomposed according to the following equations:

$$NH_4CI + HNO_3 \longrightarrow NH_4NO_3 + HCI$$
  
 $NH_4NO_3 \longrightarrow N_2O + 2H_2O$ 

# 73. Why is CaSO<sub>4</sub> not precipitated on adding ammonium sulphate to a solution containing Ca<sup>2+</sup> and Sr<sup>2+</sup> ions?

Ans.  $CaSO_4$  is not precipitated due to the formation of a complex with  $(NH_4)_2SO_4$ .  $(CH_3COO)_2Ca + (NH_4)_2SO_4 \longrightarrow CaSO_4 + 2CH_3COONH_4$   $CaSO_4 + (NH_4)_2SO_4 \longrightarrow (NH_4)_2[Ca(SO_4)_2]$ (soluble complex)

# 74. At times warming is suggested while precipitating group V cations. Explain.

Ans. The impurity of bicarbonate ion in (NH<sub>4</sub>)<sub>2</sub>CO<sub>3</sub> forms soluble bicarbonates of Ba<sup>2+</sup> and Sr<sup>2+</sup>. Warming decomposes these bicarbonates into normal carbonates which are precipitated.

$$Ca(HCO_3)_2 \longrightarrow CaCO_3 + H_2O + CO_2$$

The solution must not be boiled otherwise insoluble carbonates with ammonium chloride are converted into soluble chlorides.

$$CaCO_3 + 2NH_4Cl \longrightarrow CaCl_2 + (NH_4)_2CO_3$$

#### 75. Can we use Na<sub>2</sub>CO<sub>3</sub> in place of (NH<sub>4</sub>)<sub>2</sub>CO<sub>3</sub> in group V?

Ans. No.  $(NH_4)_2CO_3$  is a weak electrolyte and its ionisation is suppressed by the presence of  $NH_4Cl$ .  $Na_2CO_3$  is a strong electrolyte and in its solution  $[CO_3^{2-}]$  is pretty high to precipitate even MgCO<sub>3</sub> in the group V.

# 76. Why do we test group V cations in the order of Ba, Sr and Ca?

Ans. This order is selected on the basis of the following facts:

- a. Only the chromate of barium is insoluble in acetic acid whereas those of calcium and strontium are soluble in acetic acid.
- **b.** Both barium and strontium form insoluble sulphates but calcium does not.
- **c.** The oxalates of barium, strontium and calcium are insoluble.

# 77. Why is only acetic acid employed for dissolving the group V ppt?

Ans. It is due to the following reasons:

- **a.** If  $H_2SO_4$  is used,  $Ba^{2+}$ ,  $Sr^{2+}$  and  $Ca^{2+}$  will be precipitated as their sulphates.
- b. If the ppt. is dissolved either in dilute HCl or in dil. HNO<sub>3</sub>, calcium will not be precipitated by adding (NH<sub>4</sub>)<sub>2</sub>C<sub>2</sub>O<sub>4</sub> because CaC<sub>2</sub>O<sub>4</sub> formed is soluble in both dil. HCl and dil. HNO<sub>3</sub>.

However, the use of CH<sub>3</sub>COOH is free from the above difficulties. Hence it is used for dissolving the group V precipitates.

# 78. Sometimes no precipitate is obtained even if group V radicals are present. Why?

Ans. No, precipitate is obtained when the solution is dilute. In dilute solution, (NH<sub>4</sub>)<sub>2</sub>CO<sub>3</sub> hydrolyses to give carbonic acid which is a weak electrolyte. Its ionisation does not produce sufficient CO<sub>3</sub><sup>2-</sup> ion concentration to precipitate Ca, Sr and Ba as carbonates.

$$(NH_4)_2CO_3 + 2H_2O \longrightarrow 2NH_4OH + H_2CO_3$$

#### 79. Calcium oxalate is soluble in dilute HCl. Explain.

Ans. When dilute HCl is added to calcium oxalate, the oxalate ions will combine with H<sup>®</sup> ions of HCl io give feebly ionised soluble oxalic acid.

HCl 
$$\rightleftharpoons$$
 H <sup>$\oplus$</sup>  + Cl <sup>$\ominus$</sup> 

$$\downarrow COO \\ COO \\ COO \\ COO \\ COOH \\ (Feebly ionised)$$

$$\downarrow COOH \\ COOH \\ COOH \\ (Feebly ionised)$$

# 80. Why is a precipitate of magnesium carbonate not formed along with the carbonates of Ba, Sr and Ca in group V?

Ans. Magnesium requires higher concentration of CO<sub>3</sub><sup>2-</sup> ions for its precipitation as MgCO<sub>3</sub> which is insufficient in group V due to the presence of NH<sub>4</sub>Cl along with (NH<sub>4</sub>)<sub>2</sub>CO<sub>3</sub>.

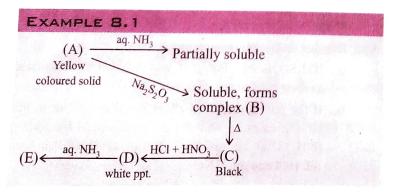
NH<sub>4</sub>Cl suppresses the ionisation of (NH<sub>4</sub>)<sub>2</sub>CO<sub>3</sub> thereby a low concentration of CO<sub>3</sub><sup>2-</sup> ions is made available due to common ion effect.

$$\begin{array}{c} \mathrm{NH_4Cl} & \Longrightarrow \mathrm{NH_4}^{\oplus} + \mathrm{Cl}^{\ominus} \\ \mathrm{(NH_4)_2CO_3} & \longleftrightarrow 2\mathrm{NH_4}^{\oplus} + \mathrm{CO_3}^{2-} \\ & \text{(common ion)} \\ & \text{(low concentration)} \end{array}$$

# 81. At times a white ppt. is obtained in group VI even in the absence of Mg. Explain.

**Ans.** The cations of group V which escape precipitation, now precipitate in group VI.

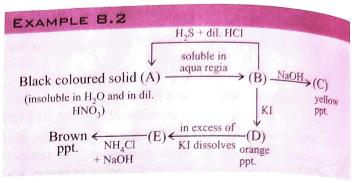
## Solved Examples



Sol. (A) is AgBr (present in photographic plate)

$$AgBr + 2Na_{2}S_{2}O_{3} \longrightarrow Na_{3}[Ag(S_{2}O_{3})_{2}] + NaBr$$
soluble
(B)
$$\downarrow \Delta$$

$$[Ag(NH_3)_2CI] \xleftarrow{NH_3} AgCI \xleftarrow{HCI + HNO_3} Ag_2S$$
(E)



Sol. (A) is insoluble in dil. HNO<sub>3</sub>.

⇒ (A) is of group II (copper sub-group) and is HgS [Only HgS (black) is insoluble in dil. HNO<sub>3</sub>]

$$(A) + 3HCl + HNO_3 \longrightarrow HgCl_2$$

$$Aqua regia$$
(B)

$$HgCl_2 + 2NaOH \longrightarrow HgO \downarrow + 2NaCl + H_2O$$
  
Yellow ppt. (C)

$$\begin{aligned} \text{HgCl}_2 + 2\text{KI} & \longrightarrow \text{HgI}_2 \downarrow + 2\text{KCl} \\ \text{(D)} \\ \text{(Orange)} \end{aligned}$$

$$HgI_2 + 2KI \longrightarrow K_2HgI_4$$
(E) (soluble)

$$NH_{4}^{\oplus} + NaOH \xrightarrow{\Delta} NH_{3} + H_{2}O + Na^{\oplus}$$

$$NH_{3} + 2K_{2}HgI_{4} \longrightarrow O \xrightarrow{Hg} NH_{2}I \downarrow$$

Brown ppt.

(iodide of Millon's base)  

$$HgCl_2 + H_2S \longrightarrow HgS + 2HCl$$

#### EXAMPLE 8.3

(A), an important laboratory reagent, turns red litmus blue, imparts golden yellow colour in flame and is a good precipitating agent. (A) reacts with Zn or Al forming H<sub>2</sub> gas. (A) gives white ppt. with ZnCl<sub>2</sub> or AlCl<sub>3</sub> but ppt. dissolves in excess of (A). What is (A) and explain reactions.

**Sol.** (A) turns blue litmus red  $\Rightarrow$  (A) is basic in nature.

- (A) imparts golden yellow colour in flame  $\Rightarrow$  (A) has Na<sup> $\oplus$ </sup>
- (A) gives  $H_2$  gas with Zn or  $Al \Rightarrow (A)$  is NaOH.

#### **Explanation:**

$$2NaOH + Zn \longrightarrow Na_2ZnO_2 + H_2 \uparrow$$

$$2NaOH + 2H_2O + 2AI \longrightarrow 2NaA1O_2 + 3H_2 \uparrow$$
 $ZnCl_2 + 2NaOH \longrightarrow Zn(OH)_2 \downarrow + 2NaC1$ 
White ppt.

 $Zn(OH)_2 + 2NaOH \longrightarrow Na_2[Zn(OH)_4] \text{ or } Na_2ZnO_2$ 
Sodium zincate
$$AlCl_3 + 3NaOH \longrightarrow Al(OH)_3 \downarrow + 3NaC1$$
White ppt.
$$A1(OH)_3 + NaOH) \longrightarrow Na[Al(OH)_4] \text{ or } NaAlO_2$$

Sodium meta-aluminate

## EXAMPLE 8.4

Identify (A) based on the following facts:

- (A) reduces HgCl<sub>2</sub> solution to white ppt. changing to grey.
- h. (A) turns FeCl<sub>3</sub> yellow coloured solution to green.
- (A) gives white ppt. with NaOH soluble in excess of NaOH.
- d. (A) gives yellow dirty ppt. on passing H<sub>2</sub>S gas, soluble in yellow ammonium sulphide (YAS).
- e. (A) gives chromyl chloride test.
- (A)gives yellow dirty ppt. soluble in YAS
  - $\Rightarrow$  (A) has  $\operatorname{Sn}^{2+}$
  - (A) gives chromyl chloride test (of  $Cl^{\Theta}$ )
  - $\Rightarrow$  (A) has  $Cl^{\Theta}$ .
  - (A) is SnCl<sub>2</sub>

#### **Explanation:**

a. 
$$\operatorname{SnCl}_2 + 2\operatorname{HgCl}_2 \longrightarrow \operatorname{Hg}_2\operatorname{Cl}_2 \downarrow + \operatorname{SnCl}_4$$

White

 $\operatorname{SnCl}_2 + \operatorname{Hg}_2\operatorname{Cl}_2 \longrightarrow 2\operatorname{Hg} + \operatorname{SnCl}_4$ 

$$2FeCl_3 + SnCl_2 \longrightarrow 2FeCl_2 + SnCl_4$$

c. 
$$SnCl_2 + 2NaOH \longrightarrow Sn(OH)_2 \downarrow + 2NaCl$$

$$Sn(OH)_2 + 2NaOH \longrightarrow Na_2SnO_2 + 2H_2O$$
Soluble

(sodium stannite)

d. 
$$\operatorname{SnCl}_2 + \operatorname{H}_2 \operatorname{S} \longrightarrow 2\operatorname{HCl} + \operatorname{SnS} \downarrow$$
Yellow

$$SnS + (NH4)2S2 \longrightarrow (NH4)2 SnS3$$

$$VAS$$
Soluble

#### EXAMPLE 8.5

# Identify A to E. (A) Scarlet salt (reddish orange) insoluble in H<sub>2</sub>O (Pink coloured) (Black ppt.) (D) (Black ppt.) (D) (Black ppt.) (D) (Black ppt.) (Dissolve in dil. HNO<sub>3</sub>

Sol. (C) is colourless soluble solution.

- (C) give black ppt. with H<sub>2</sub>S/HCl
- $\Rightarrow$  (C) is of group II
- (C) gives yellow ppt. with KI as well as with  $K_2CrO_4$
- $\Rightarrow$  (C) has Pb<sup>2+</sup>

Thus (C) is  $Pb(NO_3)_2$  obtained from (A). (B) on heating with  $Mn^{2+}$  and  $HNO_3$  gives purple colour which is due to oxidation of  $Mn^{2+}$  to  $HMnO_4$  (purple)

- ⇒ (B) is oxidising agent
- $\Rightarrow$  (B) is PbO<sub>2</sub> (blackish-brown)
- $\Rightarrow$  (A) is double oxide of lead.
- (A) is Pb<sub>3</sub>O<sub>4</sub> (red lead) (2PbO·PbO<sub>2</sub>)

$$Pb_3O_4 + 4HNO_3 \longrightarrow PbO_2 + 2Pb(NO_3)_2 + 2H_2O$$
(A) (B) (C)

$$Pb(NO_3)_2 + 2KI \longrightarrow PbI_2 \downarrow$$
(C) Yello

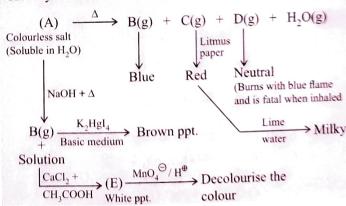
$$Pb(NO_3)_2 + K_2CrO_4 \longrightarrow PbCrO_4 \downarrow$$
Yellow

$$Pb(NO_3)_2 + H_2S \longrightarrow PbS \downarrow$$
(D) blace

$$PbO_2 + Mn^{2+} + HNO_3 \longrightarrow HMnO_4 + Pb^{2+}$$
(E) pink

#### EXAMPLE 8.6

Identify A to E.



Sol. Gas (B) gives brown ppt. with K<sub>2</sub>Hgl<sub>4</sub>

- $\Rightarrow$  gas (B) is NH<sub>3</sub>
- $\Rightarrow$  (A) has  $NH_4^{\oplus}$

Gas (C) turns lime water milky

 $\Rightarrow$  gas (C) can be  $SO_2$  or  $CO_2$ 

Gas (D) is also obtained along with (C). Gas (D) burns with blue flame and is fatal when inhaled

- ⇒. gas (D) is CO
- $\Rightarrow$  gas (C) is  $CO_2$
- $\Rightarrow$  (A) has  $C_2O_4^{2-}$

It is confirmed by the fact that CaCl<sub>2</sub> gives white ppt.  ${\rm CaC_2O_4}$  (E) which decolourises  ${\rm MnO_4}^{\ominus}\!/{\rm H}^{\oplus}$  $\Rightarrow$  (A) is  $(NH_4)_2C_2O_4$ 

#### **Explanation:**

$$(NH_4)_2C_2O_4 \xrightarrow{\Delta} 2NH_3 + CO_2 + CO + H_2O$$
(A) (B) (C) (D)

- (B) is blue towards litmus (basic)
- (C) is red towards litmus (acidic)
- (D) is neutral

$$(NH_4)C_2O_4 + 2NaOH \xrightarrow{\Delta} Na_2C_2O_4 + 2NH_3 + 2H_2O$$
(B)

$$Na_2C_2O_4 + CaCl_2 \longrightarrow CaC_2O_4 \downarrow + 2NaCl$$
White ppt.

$$NH_3 + K_2HgI_4 \longrightarrow O \xrightarrow{Hg} NH_2I \downarrow$$

$$2\text{MnO}_4^{\ \ominus} + 16\text{H}^{\oplus} + 5\text{C}_2\text{O}_4^{\ 2-} \longrightarrow 10\text{CO}_2 + 2\text{Mn}^{2+} + \text{H}_2\text{O}$$
Violet

Colourless

#### EXAMPLE 8.7

Name one common reagent that can precipitate or react and differentiate following pairs:

- a. Ag<sup>®</sup> and Ba<sup>2+</sup>
- **b.** Cu<sup>2+</sup>, Pb<sup>2+</sup>

- c.  $I^{\Theta}$  and  $CI^{\Theta}$  d.  $I^{\Theta}$  and  $Br^{\Theta}$  e.  $SO_3^{\ 2-}$  and  $SO_4^{\ 2-}$  f.  $Fe^{3+}, Cu^{2+}$
- g. Co<sup>2+</sup> and Cu<sup>2+</sup>

#### Sol.

a. 
$$K_2CrO_4$$
:  
 $2Ag^{\oplus} + CrO_4^{\ 2^-} \longrightarrow Ag_2CrO_4 \downarrow$   
 $Ba^{2^+} + CrO_4^{\ 2^-} \longrightarrow BaCrO_4 \downarrow$ 

$$Cu^{2^{+}} + CrO_{4}^{2^{-}} \longrightarrow CuCrO_{4} \downarrow$$
Chocolate
$$Pb^{2^{+}} + CrO_{4}^{2^{-}} \longrightarrow PbCrO_{4} \downarrow$$
Chocolate

c. AgNO<sub>3</sub>:

$$Ag^{\oplus} + I^{\ominus} \longrightarrow AgI \downarrow \qquad Ag^{\oplus} + CI^{\ominus} \longrightarrow AgCI \downarrow$$
Yellow White

d. Cl<sub>2</sub> water + CHCl<sub>3</sub>:

$$2I^{\ominus} + Cl_2 \longrightarrow I_2 + 2Cl^{\ominus} \qquad 2Br^{\ominus} + Cl_2 \longrightarrow Br_2 + 2Cl^{\ominus}$$
(Violet in CHCl<sub>3</sub> layer)
(Orange in CHCl<sub>4</sub> layer)

e. BaCl<sub>2</sub>:

$$BaCl_2 + SO_3^{2-} \longrightarrow BaSO_3 \downarrow$$

White ppt. soluble in conc. HCl

$$BaCl_2 + SO_4^{2-} \longrightarrow BaSO_4^{1}$$

White ppt. insoluble in conc. HCl

f. NH<sub>4</sub>SCN:  
Fe<sup>3+</sup> + SCN<sup>$$\odot$$</sup>  $\longrightarrow$  [Fe(SCN)]<sup>2+</sup>  
Red colour  
Cu<sup>2+</sup> + 2SCN <sup>$\odot$</sup>   $\longrightarrow$  Cu(SCN)<sub>2</sub> $\downarrow$ 

g. 
$$NH_4SCN$$
:  
 $Co^{2^+} + 4SCN^{\Theta} \longrightarrow [Co(SCN)_4]^{2^-}$ 
 $Cu^{2^+} + 2SC\dot{N}^{\Theta} \longrightarrow Cu(SCN)_2 \downarrow$ 
Black

#### EXAMPLE 8.8

What single reagent solution (including H2O) could be used to effect the separation of the following of solids?

- a. NaOH and Fe(OH)<sub>3</sub>
- b. Ni(OH), and Fe(OH),
- Cr<sub>2</sub>O<sub>2</sub> and Fe (OH)<sub>3</sub>
- d. MnS and CoS
- e. AgCl andAgI

#### Sol.

- a. H<sub>2</sub>O can dissolve NaOH, Fe(OH)<sub>3</sub> remains insoluble in
- **b.** NH<sub>4</sub>OH dissolves Ni(OH)<sub>2</sub>, Fe(OH)<sub>3</sub> is insoluble  $Ni(OH)_4 + 4NH_4OH \longrightarrow [Ni(NH_3)_4]^{2+}$ Soluble
- c. Excess of NaOH can dissolve Cr<sub>2</sub>O<sub>3</sub> but Fe(OH)<sub>3</sub> remains insoluble.

$$Cr_2O_3 + 3H_2O \longrightarrow 2Cr(OH)_3$$
  
 $Cr(OH)_3 + NaOH \longrightarrow Na[Cr(OH)_4]$ 
Soluble

d. Dilute HC1 dissolves MnS soluble while CoS remains insoluble.

$$MnS + 2HCl \longrightarrow MnCl_2 + H_2S \uparrow$$

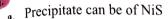
e. Aq. NH<sub>3</sub> would dissolve AgCl while AgI remains insoluble

$$AgCl + 2NH_3(aq.) \longrightarrow [Ag(NH_3)_2]Cl$$
Soluble

#### EXAMPLE 8.9

A solution may contain any of the following ions: Fe<sup>3+</sup>, Ni<sup>2+</sup>, Cr<sup>3+</sup>, Zn<sup>2+</sup>, Mn<sup>2+</sup>. Based on the experiment and results therein, indicate which of the ions would be present? Indicate any wrong information, if any. . . .

- The original solution is treated with  $(NH_4)_2S$  (a substitute of H<sub>2</sub>S) in a buffered basic solution. A dark precipitate is obtained.
- The ppt. for (a) dissolves in aqua regia.
- c. The filtrate after separating ppt. in (a) is treated with NaOH and H<sub>2</sub>O<sub>2</sub>. A dark ppt. is separated. Filtrate is colourless.
- d. The ppt. from (c) dissolves is HCl (aq.) giving a coloured solution.
- e. The solution from (d) is treated with aq. NH<sub>3</sub>. A dark ppt. forms.
- The ppt. from (e) is soluble in HCl (aq.) and solution develops an intense red colour when treated with SCN (aq.)



$$Fe^{3+} + SCN^{\odot} \longrightarrow [Fe(SCN)]^{2+}$$

- confirmed

$$Ni^{2+}$$

- probable

$$Zn^{2+}$$
,  $Mn^{2+}$ ,  $Cr^{3+}$  – absent

## EXAMPLE 8.10

Identify A to F.

$$\begin{array}{c} \text{(A)} \xrightarrow{\text{NaOH, } \Delta} \text{B(g)} \xleftarrow{\text{H}_2\text{O}} \text{Mg}_3\text{N}_2 \\ \text{Colourless salt} & + \end{array}$$

(Soluble in H2O)

Solution

FeSO<sub>4</sub> + conc. HNO<sub>3</sub>

$$\begin{array}{c}
\downarrow \\
D(g) + (E)
\end{array}$$

Brown coloured

ring (C) between two layers

(Dibasic acid)

(exist as cis. and trans. isomer)

## $(A) \xrightarrow{\text{NaOH}, \Delta} (B) \xleftarrow{\text{H}_2\text{O}} \text{Mg}_2\text{N}_2$

 $\Rightarrow$  N<sub>2</sub> has NH<sub>4</sub><sup> $\oplus$ </sup> ion and (B) is NH<sub>3</sub>

$$Mg_3N_2 + 6H_2O \longrightarrow 3Mg(OH)_2 + 2NH_3$$

$$NH_4^{\oplus} + NaOH \longrightarrow Na^{\oplus} + NH_3 + H_2O$$

Resultant solution after NH<sub>3</sub> has escaped completely contains Na<sup>®</sup> and anion of (A) which also gives Ring Test of  $NO_3^{\Theta}$ .

Thus, (A) is 
$$NH_4NO_3$$
.

$$NH_4NO_3 + NaOH \xrightarrow{\Delta} NH_3 \uparrow + NaNO_3 + H_2O$$
(A) (B)

$$NaNO_3 + H_2SO_4 \longrightarrow NaHSO_4 + HNO_3$$

$$HNO_3 \longrightarrow H_2O + NO$$

$$[Fe(H_2O)_6]SO_4 + NO \longrightarrow [Fe(H_2O)_5NO]SO_4 + [H_2O]$$

Brown coloured ring (C)

$$NH_4NO_3 \xrightarrow{\Delta} N_2O + 2H_2O$$

$$N_2O + H_2O \longrightarrow H_2N_2O_2$$
(F)

Hyponitrous acid

#### EXAMPLE 8.11

Identify (A) to (G) in the following scheme and name the process.

$$CaCO_3 \xrightarrow{\Delta} (A) + (B) gas$$
  $(A) + H_2O \longrightarrow (C)$ 

$$(A) + H_2O \longrightarrow (C)$$

$$(C) + (B) \longrightarrow CaCO_3 + H_2O$$
  $(D) + (C) \xrightarrow{\Delta} (E)$  gas

$$(D) + (C) \xrightarrow{\Delta} (E)$$
 gas

$$(E) + H_2O + (B) \longrightarrow (F)$$
  $NaC1 + (F) \longrightarrow (G) + (D)$ 

$$NaC1 + (F) \longrightarrow (G) + (D)$$

$$(G) \xrightarrow{\Delta} Na_2CO_3 + H_2O + (B)$$

Sol. Scheme represents the Solvay process of manufacture of Na<sub>2</sub>CO<sub>3</sub>.

$$CaCO_3 \xrightarrow{\Delta} CaO + CO_2(g)$$
(A) (B)

$$CaO + H_2O \longrightarrow Ca(OH)_2$$

$$(A) \qquad (C)$$

$$Ca(OH)_2 + CO_2 \longrightarrow CaCO_3 + H_2O$$

$$NH_4Cl + Ca(OH)_2 \xrightarrow{\Delta} NH_3\uparrow$$

$$NH_3 + H_2O + CO_2 \longrightarrow NH_4HCO_3$$

$$(E) \qquad (B) \qquad (F)$$

$$NaCl + NH_4HCO_3 \longrightarrow NaHCO_3 + NH_4Cl$$

$$2\text{NaHCO}_3 \xrightarrow{\Delta} \text{Na}_2\text{CO}_3 + \text{H}_2\text{O} + \text{CO}_2$$

## **Exercises**



#### Single Correct Answer Type

#### Part-A (Analysis of Anions)

- 1. Which reagent is used to remove  $SO_4^{2-}$  or  $CI^{\Theta}$  from water?
  - (1) NaOH
- (2)  $Pb(NO_3)_2$
- (3) BaSO<sub>4</sub>
- (4) KOH
- 2. Which compound will **not give** positive chromyl chloride test?
  - (1) Copper chloride, CuCl,
  - (2) Mercuric chloride, HgCl,
  - (3) Zinc chloride, ZnCl,
  - (4) Anilinium chloride, C<sub>6</sub>H<sub>5</sub>NH<sub>3</sub><sup>⊕</sup>Cl<sup>☉</sup>
- 3. A substance on treatment with dil. H<sub>2</sub>SO<sub>4</sub> liberates a colourless gas which produces (i) turbidity with baryta water and (ii) turns acidified dichromate solution green. The reaction indicates the presence of:
  - $(1) CO_3^{2-}$
- $(3) SO_{2}^{2}$
- (4) NO<sub>2</sub><sup>⊖</sup>
- 4. Conc. H<sub>2</sub>SO<sub>4</sub> on addition to dry KNO<sub>3</sub> gives brown fumes of:
  - (1) SO,
- (2) SO<sub>3</sub>

(3) NO

- (4) NO<sub>2</sub>
- 5. A white metal sulphide soluble in water is
  - (1) CuS

(2) Na<sub>2</sub>S

(3) PbS

- (4) ZnS
- 6. A salt having  $\mathrm{BO_3}^{3-}$  on burning with conc.  $\mathrm{H_2SO_4}$  gives ..... edge flame.
  - (1) Green
- (2) Yellow

(3) Red

- (4) White
- 7. KBr, on reaction with conc. H<sub>2</sub>SO<sub>4</sub>, gives reddish-brown gas:
  - (1) Bromine
- (2) Mixture of bromine and HBr

(3) HBr

- (4) NO<sub>2</sub>
- 8. An inorganic salt when heated evolves coloured gas which bleaches moist litmus paper. The evolved gas is
  - (1) NO<sub>2</sub>

(2) SO<sub>2</sub>

(3) N<sub>2</sub>O

- $(4) I_{2}$
- 9. The colour developed when sodium sulphide is added to sodium nitroprusside is
  - (1) Violet
- (2) Yellow

(3) Red

- (4) Black
- 10. Using dil. HCl, which of the following radical cannot be confirmed
  - $(1) S^{2-}$

- $(3) CO_3^{2-}$
- (2)  $S_2O_3^{2-}$ (4)  $NO_2^{\Theta}$
- 11. The solution of a chemical compound X reacts with AgNO<sub>3</sub> solution to form a white precipitate of Y which dissolves in NH<sub>4</sub>OH to give a complex Z. When Z is treated with dil. HNO<sub>3</sub>, Y reappears. The chemical compound X can be

- (1) NaCl
- (2) CH<sub>2</sub>CI
- (3) NaBr
- (4) NaT
- 12. Preparation of Na<sub>2</sub>CO<sub>3</sub> extract is made for acid radical analysis because:
  - (1) All anions react with Na to give water soluble compound
  - (2) Na is more reactive
  - (3) Na<sub>2</sub>CO<sub>3</sub> is water soluble
  - (4) None of the above
- 13. H<sub>2</sub>S and SO<sub>2</sub> can be distinguished by
  - (1) Litmus paper
- (3) Pb(CH<sub>3</sub>COO)<sub>2</sub>
- 14. Two test tubes containing a nitrate and a bromide are treated separately with H<sub>2</sub>SO<sub>4</sub> brown fumes evolved are passed in water. The water will be coloured by vapours evolved from the test tube containing:
  - (1) Nitrate
- b. Bromide
- (3) Both (a) and (b)
- (4) None of these
- 15. A solution of white crystals gives a yellow precipitate with AgNO3 but no precipitate with a solution of Na2CO3. The action of conc.  $H_2SO_4$  on the crystals yields a brown gas. The crystals are of:
  - (1) NaNO<sub>2</sub>
- (2) KCl
- (3) Ca(ON<sub>3</sub>)<sub>2</sub>
- (4) NaBr
- 16. A white precipitate insoluble in conc. HNO<sub>3</sub> is formed when aqueous solution of X in NaOH is treated with barium chloride and bromine water. The X is
  - (1) SO<sub>2</sub>

(2) SO<sub>2</sub>

(3) CO<sub>2</sub>

- (4) none of these
- 17. Aqueous solution of  $Na_2S_2O_3$  on reaction with  $Cl_2$  water gives
  - (1) Na<sub>2</sub>S<sub>4</sub>O<sub>4</sub>
- $(2) \text{ Na}_{2}\text{SO}_{4}$
- $(3) Na_2S_4O_6$
- (4) NaOH
- 18. When CS<sub>2</sub> layer containing both Br, and I, is shaken with excess of Cl<sub>2</sub> water, the violet colour due to I, disappears and a pale yellow colour appears in the solution. The disappearance of violet colour and appearance of pale yellow colour is due to the formation of:
  - (1)  $I_3^{\Theta}$  and  $Br_2$ , respectively
  - (2) HIO<sub>3</sub> and BrCl, respectively
  - (3) ICl and BrCl, respectively
  - (4)  $I^{\Theta}$  and  $Br^{\Theta}$ , respectively
- 19. Which of the following pair of acid radicals can be distinguished by using dil. H<sub>2</sub>SO<sub>4</sub>?
  - (1)  $C_2O_4^{2-}$  and  $NO_3^{\Theta}$
- (3)  $Cl^{\Theta}$  and  $Br^{\Theta}$
- (2)  $NO_3^{\ominus}$  and  $NO_2^{\ominus}$ (4)  $HCO_3^{\ominus}$  and  $CO_3^{2-}$
- 20. The aqueous solution of salt gives white ppt. with lead acetate solution which is insoluble in hot water and nitric acid. The salt contains

 $(4) SO_4^{2-}$ 

11. Some pale-green crystals are strongly heated. The gases given off are passed into a container surrounded by ice and then through a solution of acidified KMnO<sub>4</sub>. The KMnO<sub>4</sub> is decolorised, a waxy white solid is formed in the ice container; this is dissolved in water. The solution will

- (1) Give a precipitate with silver nitrate solution
- (2) Give a precipitate with barium chloride solution
- (3) Turn red litmus blue
- (4) Give blue colour with starch solution
- 22. For testing sodium carbonate solution for the presence of sulphate ions as impurities one should add:
  - (1) Excess hydrochloric acid and silver nitrate solution
  - (2) Excess sulphuric acid and silver nitrate solution
  - (3) Excess nitric acid and silver nitrate solution
  - (4) Excess hydrochloric acid and barium chloride solution
- 23. Salt A  $\xrightarrow{\text{Layer test}}$  If reddish-brown layers come first, then

(1) Br present

(2) Br<sup>⊖</sup> absent

(3) Cl<sup>©</sup> present

(4) I<sup>©</sup> present

24.  $CaCO_3(s) + CH_3COOH \xrightarrow{Na_2C_2O_4 \text{ solution}}$ ?

Comment on the product of this reaction.

- (1) No reaction
- (2) White ppt. of (CH<sub>3</sub>COO)<sub>2</sub> Ca is obtained
- (3) White ppt. of CaC<sub>2</sub>O<sub>4</sub> is formed
- (4) No ppt. is obtained

#### Part-B (Dry Tests)

- 25. The compound formed in the borax bead test of Cu<sup>2+</sup> ion in oxidising flame is
  - (1) Cu

(2) CuBO<sub>2</sub>

(3)  $Cu(BO_2)_2$ 

- (4) none of these
- 26. Potassium chromate solution is added to an aqueous solution of a metal chloride. The precipitates thus obtained are insoluble in acetic acid. These are subjected to flame test; the colour of the flame is
  - (1) Lilac

(2) Apple green

(3) Crimson red

- (4) Golden yellow
- 27. Which cation is detected by the flame test?

(1)  $NH_4^{\oplus}$ (3)  $Mg^{2+}$ 

(2) K<sup>⊕</sup>

- $(4) Al^{3+}$
- 28. Which gives violet colour with borax?
  - (1) Fe

(2) Pb

(3) Co

- (4) Mn
- 29. A green mass is formed in the charcoal cavity test when a colourless salt (X) is fused with cobalt nitrate. (X) may contain
  - (1) Aluminium

(2) Copper

(3) Barium

(4) Zinc

30. Carbonates of Ba, Sr and Ca are

(1) White

(2) Blue

(3) Green

(4) Yellow

31. The metal that does not give the borax bead test is

· (1) Cr

(2) Ni

(3) Pb

(4) Mn

- 32. Which metal gives blue ash when is salt heated with  $Na_2CO_3$ solid and Co(NO<sub>3</sub>)<sub>2</sub> on a charcoal piece?
  - (1) Cu

(2) Mg

(3) A1

(4) Zn

- 33. A minute quantity of cupric salt is heated on borax bead in reducing flame of Bunsen burner; the colour of bead after cooling will be
  - (1) Blue

(2) Red

(3) Colourless

(4) Green

34. Aqueous solution of a salt (Y) is alkaline to litmus. On strong heating, it swells-up to give a glassy material. When conc. H<sub>2</sub>SO<sub>4</sub> is added to a hot concentrated solution of (Y), white crystals of a weak acid separate out. Hence, the compound (Y)

 $(1) \text{Na}_2 \text{SO}_4 \cdot 10 \text{H}_2 \text{O}$ 

 $(2) Ca_{2}P_{6}O_{11} \cdot 10H_{2}O$ 

 $(3) \text{ Na}_{2} \text{B}_{6} \text{O}_{11}$ 

(4)  $Na_{7}B_{4}O_{7}\cdot 10H_{7}O$ 

#### Part-C (Analysis of Cations)

- 35. Strongly acidified solution of barium nitrate gives a white precipitate with ..... which did not dissolve even after large addition of water.
  - (1) Sodium phosphate

(2) Sodium carbonate

(3) Sodium sulphate

- (4) Sodium chloride
- 36. In the precipitation of the iron group in qualitative anlaysis, ammonium chloride is added before adding ammonium hydroxide to:
  - (1) Decrease concentration of  $OH^{\Theta}$  ions
  - (2) Prevent interference by phosphate ions
  - (3) Increase concentration of  $Cl^{\Theta}$  ions
  - (4) Increase concentration of  $NH_4^{\oplus}$  ions
- 37. H<sub>2</sub>S gas, on passing through an alkaline solution, forms a white precipitate. The solution contains ions of

(1) Pb

(2) Zn

(3) Cu

(4) Ni

- 38. Yellow ammonium sulphide solution is a suitable reagent used for the separation of
  - (1) HgS and PbS

(2) PbS and Bi<sub>2</sub>S<sub>3</sub>

(3)  $Bi_2S_3$  and CuS

(4) CdS and As<sub>2</sub>S<sub>3</sub>

39. An orange red precipitate obtained by passing H<sub>2</sub>S through an acidified solution of an inorganic salt indicates the presence of (1) Cadmium

(2) Tin

(3) Antimony

(4) Bismuth

**40.** Excess of concentrated sodium hydroxide can separate mixture

8.46	Inorganic Chemistry				
	(1) $Al^{3+}$ and $Cr^{3+}$	(2) $Cr^{3+}$ and $Fe^{3+}$		$(1) \text{ Co}^{2+}$	(2) $Fe^{2+}$
	(3) $Al^{3+}$ and $Zn^{2+}$	(4) $Zn^{2+}$ and $Pb^{2+}$		(3) $Ni^{2+}$	(4) Ag <sup>⊕</sup>
41	1. Which of the following sulphides has the maximum solubility			2. All ammonium salts liber	ate ammonia when:
	product?	the manning or desired,		(1) Heated with HC1	(2) Heated with caustic soda
	(1) HgS	(2) PbS	ï	(3) Heated with H <sub>2</sub> SO <sub>4</sub>	(4) Heated with NaNO,
	(3) CuS	(4) MnS	5.	3. Manganese salt + PbO <sub>2</sub> +	conc. HNO <sub>3</sub> $\longrightarrow$ The solution $h_{as}$
42.	<ul> <li>Lead has been placed in qua</li> </ul>	litative group analysis 1st and 2nd		1 .	has
	because:			The colour is due to	
	(1) It shows the valency one	e and two		$(1) \text{ HMnO}_4$	(2) A lead salt
	(2) It forms insoluble PbCl <sub>2</sub>			$(3) \operatorname{Mn(NO}_3)_2$	$(4) H_2 MnO_4$
	(3) It forms lead sulphide		54	4. An orange precipitate of	group II is dissolved in conc. HCI:
43	(4) PbCl <sub>2</sub> is partially soluble	e in water		to formation of	with excess of water turns milky $due$
73.	$As_2S_3$ is (1) Black	,		(1) Sn(OH)Cl	(2) Sb(OH)Cl <sub>2</sub>
	(3) Orange	(2) Yellow		(3) SbOCl	2
11	_	(4) White			(4) Sb(OH) <sub>2</sub> Cl
74.	A black sulphide is formed b	<del>-</del>	55	Pb( $NO_3$ ) <sub>2</sub> but not with Ba	solutions gives precipitate with
	(1) CuCl <sub>2</sub> (3) ZnCl <sub>3</sub>	(2) CdCl <sub>2</sub>		(1) Sodium chloride	(2) Sodium sulphate
45	2	(4) NaCl		(3) Sodium nitrate	
73.	may be	ble in yellow ammonium sulphide	56		(4) Sodium hydrogen phosphate ngly heated gives off brown fumes.
	(1) As, Sb, Sn	(2) Cu, Hg, Bi, Cd	5,0	A solution of this powder	gives a yellow precipitate with a
	(3) Both (a) and (b)	(4) None of these		solution of KI. When a sol	ution of barium chloride is added to
46.		used for preparation of original		a solution of powder, a wh	ite precipitate results.
	solution in analysis of basic	radicals, because it		This white powder may be	,
	(1) is oxidising agent	(2) is reducing agent		(1) A soluble sulphate	(2) KBr or NaBr
	(3) forms insoluble nitrates	(4) forms soluble nitrates		$(3) \operatorname{Ba(NO}_3)_2$	$(4) AgNO_3$
47.	The sulphide not soluble in h		57		ecipitated by both by HCl and H <sub>2</sub> S
	(1) CuS	(2) ZnS		is	
	(3) CdS	(4) HgS		(1) $Pb^{2+}$	(2) Cu <sup>⊕</sup>
48.	H <sub>2</sub> S will precipitate the sulp	hides of all the metals from the	<b>5</b> 0	(3) Ag <sup>⊕</sup>	$(4) \operatorname{Sn}^{2+}$
	solution of chlorides of Cu, Z	In and Cd if	58.		im is confirmed in the qualitative
	(1) The solution is aqueous				of a white crystalline precipitate of:
	(2) The solution is acidic			$(1) \operatorname{Mg(HCO}_{3})_{2}$ $(3) \operatorname{MgNH}_{2}(HCO_{3})$	$(2) MgNH_4PO_4$
	(3) The solution is dilute acid		50	(3) MgNH <sub>4</sub> (HCO <sub>3</sub> ) <sub>3</sub>	(4) MgCO <sub>3</sub>
	(4) Any of the above solution	•	37.	be eliminated in the appro	alysis, phosphate, if present, is to priate group in order to detect the
49.	To a solution of a substance,	gradual addition of ammonium		radical:	priate group in order to deter-
i	in excess of NH OH Howe	ecipitate which does not dissolve ver, when HCl is added to the		$(1) Pb^{2+}$	$(2) As^{3+}$
	original solution, a white pre-	cipitate is formed. The solution		(3) $Ca^{2+}$	(4) $Cd^{2+}$
	contained	orprise is refined. The solution	60.		in place of $(NH_4)_2CO_3$ for the
(	1) Lead salt	(2) Silver salt		precipitation of group V be	cause
(	3) Mercurous salt	(4) Copper salt		(1) Na <sup>⊕</sup> interferes in the de	tection of group V
<b>50.</b> A	A compound is soluble in water	: If ammonia is added to aqueous		(2) Concentration of CO <sub>3</sub> <sup>2-</sup>	is very low
		rown precipitate appears which		(3) Na will react with acid	
is	s soluble in dil. HCl. The con	npound has		(4) Mg will be precipitated	
(1	1) Aluminium	(2) Zinc	61.	Disodium hydrogen phosph	
(3	3) Iron	(4) Cadmium		(1) Mg <sup>2+</sup>	(2) Na <sup>⊕</sup>
		soluble in water gives black		(3) $Ca^{2+}$	(4) All of these
_	<del>-</del>	ch dissolves readily in HCl. The	62.	Reddish-brown (chocolate)	
m	etal ion present is			(storate)	rr

(2)  $Ba^{2+}$  and  $SO_4^{2-}$ 

(1) Cu<sup>2+</sup> and Fe(CN)<sub>6</sub><sup>4-</sup> (3)  $Pb^{2+}$  and  $I^{\Theta}$ 

(4) None of these

Addition of SnCl<sub>2</sub> to HgCl<sub>2</sub> gives ppt.:

(1) White turning to grey

(2) Black turning to white

(3) White turning to red

(4) None of these

To avoid the precipitation of hydroxides of  $Ni^{2+}$ ,  $Co^{2+}$ ,  $Zn^{2+}$  and  $Mn^{2+}$  along with those of  $Fe^{3+}$ ,  $Al^{3+}$  and  $Cr^{3+}$  the third group solution should be

(1) Heated with a few drops of conc. HNO,

(2) Treated with excess of NH<sub>4</sub>Cl

(3) Concentrated

(4) None of these

65. Which gives a white precipitate with a solution of AgNO<sub>3</sub>, a white precipitate with dil. H<sub>2</sub>SO<sub>4</sub>, and a green flame test?

(1) Copper chloride

(2) Copper nitrate

(3) Lead nitrate

(4) Barium chloride

66. In qualitative inorganic analysis of basic radicals, hydrochloric acid is preferred to nitric acid for preparing a solution of given substance. This is because:

(1) Nitrates are not decomposed to sulphides

(2) Nitric acid contains nitrogen

(3) Hydrochloric acid is not an oxidising agent

(4) Chlorides are easily converted to sulphides

67. Addition of solution of oxalate to an aqueous solution of mixture of Ba<sup>2+</sup>, Sr<sup>2+</sup> and Ca<sup>2+</sup> will precipitate:

(1)  $Ca^{2+}$ 

(2)  $Ca^{2+}$  and  $Sr^{2+}$ 

(3)  $Ba^{2+}$  and  $Sr^{2+}$ 

(4) All the three

68. The reagent that distinguishes between silver and lead salt is

(1) H<sub>2</sub>S gas

(2) dil. HCl solution added after this dissolved in hot water

(3) NH<sub>4</sub>Cl (solid) + NH<sub>4</sub>OH (solution)

(4)  $NH_4Cl$  (solid) +  $(NH_4)_2CO_3$  solution

**69.** Sulphide ions react with  $Na_2[Fe(NO)(CN)_5]$  to form a purple coloured compound Na<sub>4</sub>[Fe(CN)<sub>5</sub>(NOS)]. In the reaction, the oxidation state of iron;

(1) Changes from + 2 to +3 (2) Changes from +3 to +2

(3) Changes from +2 to +4

(4) Does not change

70. The product of reaction of an aq. solution of Bi<sup>3+</sup> salt with sodium thiosuiphate gives:

(1) BiS

(2)  $Bi_2(S_2O_3)_3$ 

(3) Na[Bi( $S_2O_3$ )<sub>2</sub>]

(4)  $[Bi_2(S_2O_3)_2]Cl_2$ 

→ B + C (Filtrate)  $(A) + HClO_4$ 71. White ppt. NaOH (Mix. of Brown ppt.  $\leftarrow_{K_2\text{Hgl}_4/\text{OH}^{\odot}} D$ two cation)

The cations present in A are

(1)  $K^{\oplus}$  and  $Na^{\oplus}$ 

(3)  $\mathrm{NH_4}^\oplus$  and  $\mathrm{Fe}^{2^+}$ 

(2)  $K^{\oplus}$  and  $NH_4^{\oplus}$ (4)  $Mg^{2^+}$  and  $Na^{\oplus}$ 

72. Few drops of  $HNO_3$  are added to group II before proceeding to group III in order to:

Part-D (Miscellaneous)

**78.** Prussian blue is formed when:

(1) Ferrous sulphate reacts with FeCl<sub>3</sub> (2) Ferric sulphate reacts with  $K_4[Fe(CN)_6]$ 

Salt is consisting of cations:

X

 $Pb(NO_3)_2$ 

 $AgNO_3$ 

AgNO<sub>3</sub>

AgNO<sub>3</sub>

**76.** Salt mixture  $\xrightarrow{\text{dil. HCl}}$  White ppt.

Y

 $NO_{2}$ 

NO

NO,

NO,

(1)  $Pb^{2+}$  and  $Hg^{2+}$ 

Heated and

filtered under

hot condition

(3) ppt. group III

(1) Iodine crystals

(1) FeCl<sub>3</sub>

(3) SnCl<sub>2</sub>

(1)

(2)

(3)

(4)

(2)  $Pb^{2+}$  and  $Hg_2^{2+}$ 

 $\rightarrow$  Residue  $\xrightarrow{NH, sol.}$  Clear

 $[Ag(NH_3)_2]^{\oplus}$ 

(3)  $Pb^{2+}$  and  $Ag^{\oplus}$ 

(4)  $Pb^{2+}$ , Hg, Hg, Hg and Hg

→ Filtrate Cooled → White needle

like crystal

Na,  $[Hg(S_2O_3)_2]$ 

77.  $Hg(NO_3)$ ,  $\xrightarrow{\Delta} W + X + O$ ,

$$X + H_2O \longrightarrow HNO_2 + HNO_3$$

$$W + HNO_3 \longrightarrow Y + NO + H_2O$$

$$Y + Na_2S_2O_3(excess) \longrightarrow Z + NaNO_3$$

W X (1) Hg,  $Hg(NO_3)$ ,  $N_2O_2$ 

NO, Na  $[Hg(S_2O_3)_2]$ (2) HgO,  $Hg(NO_3)_3$ 

(3) Hg,  $Hg(NO_3)_3$ Na,  $[Hg(S_2O_3)_2]$ NO<sub>2</sub>,

(4) Hg,  $Hg(NO_3)_7$  $Na_{3} [Hg(S_{2}O_{3})_{2}]$  $N_{2}O_{2}$ 

- (3) Ferrous ammonium sulphate reacts with FeCl<sub>3</sub>
- (4) Ammonium sulphate reacts with FeCl<sub>3</sub>
- 79. A metal salt solution forms a yellow precipitate with potassium chromate in acetic acid, a white precipitate with dil. sulphuric acid, but gives no precipitate with sodium chloride or iodide. The white precipitate obtained when sodium carbonate is added to the metal salt solution consists of
  - (1) Lead carbonate
- (2) Basic lead carbonate
- (3) Barium carbonate
- (4) Strontium carbonate
- 80. Chemical volcano is produced on heating:
  - $(1) K_{2}Cr_{2}O_{7}$
- $(2) (NH_4)_2 Cr_2 O_7$
- (3) ZnCr<sub>2</sub>O<sub>7</sub>
- $(4) K_2 CrO_4$
- 81. A  $\rightarrow$  $B + C_{(g)} + D_{(g)}$ (Solid) Brown residue) Aqueous NaOH

E(dirty green precipitate)  $\xrightarrow{\text{On exposure}}$  F Identify A.

- (1) FeCl<sub>3</sub>
- (2)  $Fe_2(SO_4)_3$
- (3) FeSO<sub>4</sub>
- (4) All are correct
- aq. solution → BaCl, in  $(D) \leftarrow (A)$ White ppt. presence of HCl (Light green) with K<sub>2</sub>HgI<sub>4</sub> Brown ppt. crystalline compound

Aqueous solution with 
$$K_3[Fe(CN)_6]$$
(C)
Blue

Identify A.

- (1) FeSO<sub>4</sub>
- $(2) (NH_4)_2 SO_4$
- $(3) \ FeSO_4(NH_4)_2SO_4.6H_2O \quad (4) \ All \ are \ correct$
- **83.** Fe + conc.  $HNO_3 \longrightarrow X$ . Then X will be (> 80%)
  - (1)  $Fe_2O_3$
- (2) FeO
- $(3) \operatorname{Fe}_3 O_4$
- (4) None of these
- 84. Yellow coloured solution of FeCl<sub>3</sub> changes to light green when:
  - (1) SnCl<sub>2</sub> is added
- (2) Zn is added
- (3) H<sub>2</sub>S gas is passed
- (4) All true
- **85.**  $Fe^{2+}$  does not give blue colour with  $K_4[Fe(CN)_6]$  but on its reaction with (X), blue colour appears. (X) can be:
  - $(1)\, MnO_4^{\,\, \ominus}/\, H^\oplus$
- (2) H<sub>2</sub>SO<sub>4</sub>
- (3) NH<sub>3</sub>
- (4) HC1
- **86.**  $Fe(OH)_3$  and  $Cr(OH)_3$  ppt. are separated by
  - (1) Aq. NH<sub>3</sub>
- (2) HC1
- (3) NaOH /  $H_2O_2$
- (4) H<sub>2</sub>SO<sub>4</sub>
- 87. Turnbull's blue and Prussian's blue respectively are Fe<sup>II</sup>[Fe<sup>II</sup>(CN)<sub>2</sub>]<sup>2-</sup>

$$Fe^{II}[Fe^{II}(CN)_{6}]^{2-} Fe^{III}[Fe^{III}(CN)_{6}]$$

$$I$$

$$Fe^{II}[Fe^{III}(CN)_{6}]^{\Theta} Fe^{III}[Fe^{III}(CN)_{6}]^{\Theta}$$

(1) I, II

(2) I, III

- (3) III, IV
- (4) IV, III
- 88. Which of the following are soluble in excess of NaOH (X): As<sub>2</sub>S<sub>3</sub> (Y): CuS; (Z): AlCl<sub>3</sub>:
  - (1) X, Y, Z
- (2) Y, Z
- (3) X, Z
- (4) X, Y
- 89. A mixture on heating gave a gas used as an anaesthetic, soluble in water forming cis., and trans. dibasic acid 1.1 g of gas occupies 0.56 L at STP. Mixture contains
  - (1)  $NaNO_3 + NH_4CI$
- (2)  $NaNO_2 + NH_4Cl$
- (3) CaCO<sub>3</sub> + MgCO<sub>3</sub>
- (4)  $NH_4C1 + Na_2SO_4$
- 90. Aq. solution contains Zn(CH<sub>3</sub>COO)<sub>2</sub>, Cd(CH<sub>3</sub>COO)<sub>2</sub> and Cu(CH<sub>3</sub>COO)<sub>2</sub>. On passing H<sub>2</sub>S gas, there is precipitation of ..... as sulphide:
  - $(1) Zn^{2+}, Cd^{2+}$
- (2)  $Cu^{2+}$ ,  $Cd^{2+}$
- (3)  $Zn^{2+}$ ,  $Cu^{2+}$
- (4) Zn<sup>2+</sup>, Cu<sup>2+</sup>, Cd<sup>2+</sup>
- 91. Ferric alum gives red colour with NH<sub>4</sub>SCN due to formation
  - $(1) Al(SCN)_3$
- (2) [Fe(SCN)<sub>3</sub>]<sup>⊙</sup>
- $(3) \text{ Fe(SCN)}_3$
- (4) [Fe(SCN)]<sup>2+</sup>
- **92.** Colourless salt  $(X) \xrightarrow{\Delta} (Y) \xrightarrow{Cu^{2+}, \Delta}$  coloured bead (Z)(X) can be
  - (1) borax
- (2) micro-cosmic salt

- (3) both
- (4) none
- 93. KCl + conc.  $H_2SO_4 + K_2Cr_2O_7 \xrightarrow{\Delta} (X) \xrightarrow{NaOH} (Y)$ .
  - (X) is reddish brown coloured gas soluble in NaOH forming (Y). (X) and (Y) are
  - (1) Cr<sub>2</sub>OCl<sub>2</sub>, Na<sub>2</sub>CrO<sub>3</sub>
- (2) Cr<sub>2</sub>O<sub>2</sub>Cl<sub>2</sub>, Na<sub>2</sub>CrO<sub>2</sub>
- (3) CrO<sub>2</sub>Cl, Na<sub>2</sub>CrO<sub>4</sub>
- (4) CrO,Cl,, Na,CrO,
- 94. Aqueous solution of BaBr<sub>2</sub> gives yellow ppt. with
  - $(1) K_2 CrO_4$
- (2) AgNO<sub>3</sub>
- (3) both
- (4) none
- 95.  $\operatorname{Cr}_{2}\operatorname{O}_{7}^{2-} \xrightarrow{\operatorname{pH} = x} \operatorname{CrO}_{4}^{2-}$ .

This change is based on change in pH. Probable values of x and y can be

- (1) 8, 6
- (2) 8, 10
- (3)4,6
- (4) change is independent of pH
- **96.**  $H_2S$  would separate the following in pH < 7:
  - (1)  $Zn^{2+}$ ,  $Co^{2+}$
- (2)  $Cu^{2+}$ ,  $Cd^{2+}$
- (3)  $Cu^{2+}$ ,  $Cr^{3+}$
- (4)  $Cu^{2+}$ .  $As^{3+}$
- 97. Solution of (X) in dil.  $HCl + H_2O \longrightarrow$  white turbidity. (X)  $\xrightarrow{\text{H}_2\text{S/HCl}}$  black ppt. (Y). (Y) is soluble in
  - (1) NaOH
- (2) YAS
- (3) HNO<sub>3</sub>
- (4) HCl

		•
98.	K <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub> + conc. H <sub>2</sub> SO <sub>4</sub> - nerchromic anhydride (in ethe	$+ H_2O_2 + \text{ether} \longrightarrow \text{blue}$ ereal layer). Blue colour is due
	to	
		(2) H <sub>2</sub> CrO <sub>4</sub>
	$_{(3)}$ H <sub>2</sub> Cr <sub>2</sub> O <sub>3</sub> (	(4) CrO <sub>5</sub>
	There is foul smell in present	ce of moisture with
99.	(1) AlCl <sub>3</sub>	$(2) \operatorname{Al}_{2}(\operatorname{SO}_{4})_{3}$
	(3) FeS	$(4) \operatorname{FeSO}_{4}$
)0.	some time. Black ppt. is of	hypo changing to black after
	$(1) Ag_2S_2O_3$	$(2) Ag_2SO_4$
	$^{(3)}Ag_2S_4O_6$	(4) Ag2S
<b>01.</b>	$K_2Cr_2O_7/H^{\oplus}$ (B) green while	water (A) milky, SO <sub>2</sub> also turns e O <sub>2</sub> is soluble in pyrogallol (C) is are to be detected in order by der is
	(1)(A), (B), (C)	(2)(B),(C),(A)
	(3)(B),(A),(C)	(4)(A),(C),(B)
02.	converted into soluble sodi in the preparation of sodiu	slightly insoluble in water. It is um sulphate by using Na <sub>2</sub> CO <sub>3</sub> im carbonate extract. Mole of lete conversion of 1 mole of (X)
	(1) 1	(2) 2
	(3) 3	(4) 4
03.	. CoCl. gives blue colour wi	th NH <sub>4</sub> SCN due to formation of
	$(1) (NH_4)_2 [Co(SCN)_4]$	(2) (NH4)4[Co(SCN)6]
	(3) $(NH_4)_3$ [Co(SCN) <sub>6</sub> ]	$(4) (NH_4) (Co(SCN)_4]$
	(3) (1114/3 [33(23)]	$\rightarrow$ (A) $\longrightarrow$ (B).
04	. HgCl <sub>2</sub> + excess of KI —	NH <sub>3</sub>
	(A) and (B) respectively ar	Hg
	(A) and (B) respectively at (1) K <sub>2</sub> HgI <sub>4</sub> (Nesslers reage	ent) $O \stackrel{\text{NH}_2}{\longrightarrow} 1$
	$(X) = 2^{-2} \mathcal{S} + (X)$	(Iodide of Millon's base)
		(Y)
	(2)(Y),(X)	
	(3) both (X)	
		3+ ~ 2+
104	NU SCN can be used to te	est one or more out of Fe <sup>3+</sup> , Co <sup>2+</sup> ,
- 0,	Cu <sup>2+</sup>	21 - 2+
	(1) $Fe^{3+}$ only	(2) $Co^{2+}$ , $Cu^{2+}$
	21	(4) all
10	6 V (Ea(CN) 1 can be use	d to detect one or more out of
	$Fe^{2+}$ , $Fe^{3+}$ , $Zn^{2-}$ , $Cu^{-}$ , $Cu^{-}$	(2) $Fe^{3+}$ , $Zn^{2+}$ , $Cu^{2+}$
	(1) $Fe^{2+}$ , $Fe^{3+}$	(4) all but Fe <sup>27</sup>
1.	(3) all but Fe <sup>3+</sup>	(4) an out 1.
10	7. Aqueous solution of bora This is because of	cp(OH) only

(1) formation of 2 mol. of  $B(OH)_3$  only (2) formation of 2 mol. of  $[B(OH)_4]^{\Theta}$  only

- (3) formation of 1 mol. each of B(OH)<sub>3</sub> and  $[B(OH)_4]^{\odot}$ (4) formation of 2 mol. each of  $[B(OH)_4]^{\odot}$  and  $B(OH)_3$ , of which only  $[B(OH)_{4}]^{\Theta}$  reacts with acid 108. Ag<sub>2</sub>S is soluble in NaCN due to formation of (1) Na[Ag(CN)<sub>2</sub>]  $(2) Ag(CN)_2$ (4)  $Na_{2}[Ag(CN)_{2}]$  $(3) \text{Na}_2[\text{Ag}(\text{CN})_3]$ 109. A compound gives violet flame test and gives a white ppt. With AgNO<sub>3</sub>, The compound is (2) KCl (1) NaCl (4) CaCl<sub>2</sub> (3) BaCl<sub>2</sub> 110. Bromine vapours turns ..... paper blue. (1) Starch iodide (2) Starch (4) Methyl orange (3) Lead acetate 111. Solution of a salt in sulphanilic acid and  $\alpha$ -naphthylamine give red ppt., due to (2) I<sup>⊖</sup>
  (4) NO<sub>3</sub><sup>⊖</sup> (1) Br<sup>⊖</sup> (3) NO₂<sup>⊖</sup> 112. Solution of a salt in dil. H<sub>2</sub>SO<sub>4</sub> produces deep blue colour with starch iodide solution. The salt contains (2) I<sup>⊖</sup> (1) Br<sup>⊖</sup> (4) NO₃<sup>⊖</sup> (3) NO₂<sup>⊖</sup> 113. The gas which turns mercurous nitrate paper black is (2) Cl<sub>2</sub>(1) NH<sub>3</sub>(4) SO<sub>3</sub>(3) SO<sub>2</sub>114. A mixture when heated with dil. H<sub>2</sub>SO<sub>4</sub> does not evolve  $(1) NO_2^{\Theta}$ (3) I<sup>⊖</sup>
  - brown vapours but with conc. H<sub>2</sub>SO<sub>4</sub> brown vapours are obtained. The vapours when brought in contact with AgNO, soln. do not give any precipitate. The mixture contains.
  - 115. To solution of a salt in acid medium, AgNO3 is added, a white ppts. rapidly changing to yellow orange, brown and finally black is obtained. This is due to the presence of
    - $(1) SO_3^{2-}$
- $(2) \, {\rm S_2O_3}^{2-}$
- (3) CH<sub>3</sub>COO<sup>©</sup>
- $(4) S_2^{\ominus}$
- 116. Nitrite and nitrate both respond to ring test. Nitrites are removed by treating with
  - (1) Conc. HNO<sub>3</sub>
- (2) NH<sub>4</sub>Cl
- (3) Conc H<sub>2</sub>SO<sub>4</sub>
- (4) MnO<sub>2</sub>
- 117. Which of the following metal oxides is white in colour but becomes yellow on heating
  - (1) AgO

(2) ZnO

- (3) Ag<sub>2</sub>O
- (4) FeO
- 118. Chromyl chloride test is preformed for the detection of Cl<sup>Θ</sup>. A salt solution containing Cl<sup>Θ</sup> ion is heated with  $K_2Cr_2O_7$  and conc.  $H_2SO_4$ , orange red vapours of  $CrO_2Cl_2$ are obtained. On passing these vapours through a soln. of NaOH, a yellow ppt. due to Na2CrO4 is obtained. If these

126.

127.

(3) Sn

(4) Hg

3.50	Inorganic Chemistry				
	vapours are dissolved i solution is added then	n H <sub>2</sub> O and acetic acid and lead acetate	128.	A white ppt. ob becomes black or	tained in the analysis of a mixture treatment with NH <sub>3</sub> or NH <sub>4</sub> OH due to finely divided Hg and Hg (NH) or
	(1) The solution will remain colour less				
	(2) The solution will b	oecome dark green			I] The salt may be (2) AgCl
	(3) The solution will	become brown		(1) PbCl <sub>2</sub>	· -
	(4) A yellow ppt. will	be obtained	120	(3) HgCl <sub>2</sub>	(4) Hg <sub>2</sub> Cl <sub>2</sub>
119.	-	test responds poorly with the chlorides but fails with the chlorides of	129.	solution (1) Ni <sup>2+</sup>	wing ions will give a colourless aqueout $(2) Cu^{\oplus}$
	(1) Hg	(2) As		(1) $NI$ (3) $Cu^{2+}$	(4) Fe <sup>2+</sup>
	(3) Bi	(4) Cu	120		
120.	When a salt is heated	l with dil. H <sub>2</sub> SO <sub>4</sub> and KMnO <sub>4</sub> soln.,	130.		owing is insoluble in dil. HNO <sub>3</sub>
		MnO <sub>4</sub> is discharged, the mixture may		(1) HgS	(2) PbS
	contain			$(3) \operatorname{Bi}_{2} S_{3}$	(4) CuS
	(1) Sulphite	(2) Carbonate	131.		owing sulphate is insoluble in H <sub>2</sub> O
	(3) Nitrate	(4) Bicarbonate		(1) CuSO <sub>4</sub>	(2) PbSO <sub>4</sub>
121.		is confirmed by acidifying the soda		(3) CdSO <sub>4</sub>	$(4) \operatorname{Bi}_{2}(\operatorname{SO}_{4})_{3}$
		ion and then adding freshly prepared	132.		e minimum solubility product?
		ring is formed due to the formation of This test should not be performed for		(1) AgCl	(2) AlCl3
	nitrate ion in presence		6.0	(3) BaCl <sub>2</sub>	(4) NH <sub>4</sub> Cl
	(1) $NO_2^{\odot}$ (2) $Br^{\odot}$		133.	When H <sub>2</sub> S is passe	ed through an ammonical salt solution X
	(3) I <sup>©</sup>	(4) All			tained. The X can be a
122		solution is acidified with excess of dil.		(1) Cobalt salt	(2) Zinc salt
		soln. is added. A white ppt. insoluble	124	(3) Nickel salt	(4) Manganese salt
	in CH <sub>3</sub> COOH confirms.		134.		e(CN) <sub>6</sub> ] <sup>4</sup> gives a ppt. of
	$(1) C_2 O_4^{2-}$	$(2) CO_3^{2-}  (4) S_2O_3^{2-}$		2	pric ferro cyanide)
	$(3) \text{HCO}_3^{\Theta}$	$(4) S_2 O_3^{2-}$		(1) Blue	(2) Green
123	3. When Cl <sub>2</sub> water is add	led to an excess soln. of KI in presence	125	(3) Chocolate	(4) White
	of CHCl <sub>3</sub> , a violet co	plour is obtained. On adding more of	135.		$[e(CN)_6]^{3-}$ gives a ppt. of
	water, the violet color	ir disappears and a colourless solution		$Co_3$ [Fe(CN) <sub>6</sub> ].	(2) D - 11'-1 1
	_	confirms the presence of		(1) Blue	(2) Reddish brown
	(1) I <sup>⊖</sup>	(2) Br <sup>⊖</sup>	126	(3) Chocolate	(4) Green
	(3) Cl <sup>⊖</sup>	(4) $I^{\Theta}$ and $Br^{\Theta}$	130.		H <sub>4</sub> SCN gives ppt. of
124		nt is dil. HCl, which of the following			which is soluble in acetone.
	<b>do not</b> belong to grou	-		(1) Blue	(2) Green
	(1) Ag <sup>⊕</sup>	(2) $Pb^{2+}$	125	(3) Chocolate	(4) Reddish brown
	(3) $Hg_2^{2+}$	$(4) \text{ Hg}^{2+}$	137.	_	I in groups I and II because lency of one and two
125.		g is not precipitated by H <sub>2</sub> S in presence		(2) It is partly solu	•
	of NH <sub>3</sub>	2.		(3) It forms insolul	-
	(1) $Co^{2+}$	(2) $Mn^{2+}$		(4) It forms lead su	ılphide
	(3) $Fe^{3+}$	$(4) \text{ Cd}^{2+}$	138.	With Fe <sup>3+</sup> ions	[Fe(CN) <sub>6</sub> ] <sup>4-</sup> gives Prussian blue
126.	A white ppt. obtained	in the analysis of a mixture becomes		colouration due to	the formation of ferri-terro cyanius
	black on treatment wi	th NH <sub>4</sub> OH. It may be		re <sub>4</sub> [Fe(CN) <sub>6</sub> ] <sub>3</sub> whill colouration	le with NH <sub>4</sub> SCN, Fe <sup>3+</sup> ion gives
	$(1) \operatorname{Hg_2Cl_2}$	(2) HgCl <sub>2</sub>			(2) Blue
	(3) PbCl <sub>2</sub>	(4) AgCl		(1) Deep red	(4) Green
127.	When excess of SnCl <sub>2</sub>	is added to a soln. of HgCl <sub>2</sub> , a white	120	(3) Brown	on heating with $K_2Cr_2O_7$ gives a yellow
		stained the grey colour is due to the	137.	ppt. insoluble in ac	eetic acid. The metal may be
	$(1) \operatorname{Hg}_2 \operatorname{Cl}_2$	(2) SnCl <sub>4</sub>		(1) Hg	(2) Zn (4) Ag
	_			1 1 1 1 1 1 1	171/12

147. I

(4) Ag

(3) Pb

- 162. Orange coloured sodium cobaltinitrite  $Na_3[Co(NO_2)_6]$  is used for the detection of  $K^{\oplus}$  ions which gives ...... ppt. due to the formation of Pot. Sod. Cobaltinitrite  $K_2Na[Co(NO_2)_6]$ 
  - (1) White
- (2) Orange
- (3) Yellow
- (4) Brown

#### **Multiple Correct Answers Type**

#### Part-A (Analysis of Anions)

- 1. When Zn reacts with conc. HNO<sub>3</sub>, then Zn(NO<sub>3</sub>) and NO<sub>2</sub> are formed; the reaction(s) involved in this process is/are
  - (1) Redox reaction
- (2) Acid-base reaction
- (3) Ion exchange reaction
- (4) None
- 2. Select the correct statement(s):
  - (1) NaHCO<sub>3</sub> is sparingly soluble in water because it has massive H-bonding.
  - (2) When BaCl<sub>2</sub> reacts with bicarbonate, then white ppt. of BaCO<sub>3</sub> is formed.
  - (3) HgCl<sub>2</sub> is poisonous
  - (4) Phenophthalein is turned pink by soluble carbonate and colourless by soluble hydrogen carbonate.
- **3.** Which of the following anions may be identified by their ppt. reaction in aqueous solution?
  - (1)  $CrO_{4}^{2-}$
- $(2) SO_4^{2}$
- (3)  $PO_4^{3-}$
- (4) MnO₄<sup>∈</sup>
- **4.** Select the correct statement(s):
  - (1) White ppt. of BaSO<sub>3</sub> and CaSO<sub>3</sub> is soluble in dil. HNO<sub>3</sub>, dil. HCl and CH<sub>3</sub>COOH.
  - (2) On standing, the precipitate BaSO<sub>3</sub> is slowly oxidised to sulphate and then becomes insoluble in dilute mineral acids.
  - (3) When excess of SO<sub>2</sub> gas is passed into the solution of BaSO<sub>3</sub> and CaSO<sub>3</sub>, then white turbidity disappears.
  - (4) The hydrogen carbonates of alkali metals are soluble in water, but are less soluble than the corresponding normal carbonates.
- **5.** Which of the following carbonates do not give metal oxide on heating?
  - (1) CuCO<sub>3</sub>
- (2) K<sub>2</sub>CO<sub>3</sub>
- (3) Na<sub>2</sub>CO<sub>3</sub>
- (4) MgCO<sub>3</sub>
- 6. Which of the following compounds are soluble in water?
  - $(1) CaC_2O_4$
- (2) SrSO<sub>4</sub>
- (3) BaCl<sub>2</sub>
- $(4) (NH_4)_2 C_2 O_4$
- 7. Which of the following halides are not soluble in water?
  - (1) AgCl
- (2) AgBr
- (3) PbCl<sub>2</sub>
- (4) AgF
- **8.** The brown ring test is performed for the qualitative detection of
  - (1) Bromides
- (2) Iodides
- (3) Nitrates
- (4) Nitrite

- 9. Which of the following salt does give positive test for nitrate ion?
  - (1) KNO<sub>3</sub>
- (2) NaNO<sub>3</sub>
- $(3) \text{ Mg(NO}_3)_2$
- (4) None of these
- 10. Which of the following anions are easily removed from aqueous solution by precipitation?
  - (1) Cl<sup>Θ</sup>

- (2)  $SO_4^{2-}$
- (3) NO<sub>3</sub><sup>⊖</sup>
- $(4) CO_3^{2-}$
- 11. A white ppt. is obtained when:
  - (1) A solution of BaCl<sub>2</sub> is treated with Na<sub>2</sub>CO<sub>2</sub>
  - (2) A solution of CaCl<sub>2</sub> is treated with Na<sub>2</sub>SO<sub>2</sub>
  - (3) A solution of ZnSO<sub>2</sub> is treated with Na<sub>2</sub>S
  - (4) A solution of Pb(NO<sub>3</sub>)<sub>2</sub> is treated with Na<sub>2</sub>CrO<sub>4</sub>
- **12.** Which pair would not be expected to form precipitate when solutions are mixed?
  - $(1) K^{\oplus}, SO_4^{2-}$
- (2) Na $^{\oplus}$ , S<sup>2-</sup>
- $(3) Ag^{\oplus}, NO_3^{\ominus}$
- $(4) \text{ Al}^{3+}, \text{ OH}^{\Theta}$
- 13. Reddish brown gas is obtained when the following are treated with conc.  $H_2SO_4$ .
  - $(1) \operatorname{Br}^{\Theta}$

- $(2) NO_2^{\Theta}$
- $(3) NO_3^{\Theta}$
- $(4) SO_3^{2-}$
- **14.** The correct statement(s) is/are with respect to chromyl chloride test:
  - (1) Formation of lead chromate
  - (2) Formation of chromyl chloride
  - (3) Liberation of chloride
  - (4) Formation of reddish-brown vapours.
- 15. Nitrite  $(NO_2^{\odot})$  interfers in the 'ring-test' of nitrate  $(NO_3^{\odot})$ . Some of the following reagents can be used for the removal of nitrite.
  - (1) AgF
  - (2) (NH<sub>2</sub>)<sub>2</sub> CS (thiourea)
  - (3) NH<sub>2</sub>SO<sub>3</sub>H (sulphanilic acid)
  - (4) None of these
- **16.** If (X) turns lime water milky, then X may be
  - $(1) CO_{2}$

(2) SO<sub>2</sub>

- (3) NO<sub>2</sub>
- $(4) O_{2}$
- 17. If (X) turns acidified  $K_2Cr_2O_7$  solution green, then X may be
  - (1) SO<sub>2</sub>

- (2) CO<sub>2</sub>
- $(3) NO_2^{\Theta}$
- (4)  $Fe^{2+}$
- **18.** If (X) decolourises acidified KMnO<sub>4</sub> solution, then X may be
  - $(1) S^{2-}$

 $(2) SO_3^{2-}$ 

(3)  $Fe^{2+}$ 

- (4) SO<sub>2</sub>
- **19.** Which of the following ppt. (s) of sulphite ion have white colour?

(1) Ag<sub>2</sub>SO<sub>3</sub> (4) BaSO, (3) CaSO<sub>3</sub>

Which of the following gases have brown colour?

(2) NO<sub>2</sub>(1) Br<sub>2</sub>  $(4) I_{2}$ (3)  $CO_2$ 

 $S^{2}$  and  $SO_3^{2-}$  can be distinguished by using:

(1) (CH<sub>3</sub>COO)<sub>2</sub>Pb

(2) Na<sub>2</sub>[Fe(CN)<sub>5</sub>NO]

 $(3) \operatorname{Cr}_2 \operatorname{O}_7^{2-}$  solution (4) CaCl<sub>2</sub> 12. Consider the following reaction:

Nitrite + acetic acid + thiourea  $\longrightarrow$  N<sub>2</sub> + SCN + 2H<sub>2</sub>O Formation of the product in the above reaction cannot be identified by

(1) FeCl<sub>3</sub>/dil. HCl when blood-red colour appears

(2) FeCl<sub>3</sub>/dil. HCl when blue colour appears

(3) K,Cr<sub>2</sub>O<sub>7</sub>/HCl when green colour appears

(4) KMnO<sub>4</sub>/HCl when colourless solution is formed

Purple colour of KMnO<sub>4</sub> 23. KMnO₄ ₹ decolourises Br-

Brown colour of Br, water water become colourless

The gas will be

(2) SO<sub>2</sub>(1) CO<sub>2</sub>

(4) SO<sub>3</sub>(3) H<sub>2</sub>S

24. Which of the following combinations in an aqueous medium will give a yellow ppt.?

 $(1) AgNO_3 + NaBr$ 

(2) Pb(CH<sub>3</sub>COO)<sub>2</sub> + Na<sub>2</sub>CrO<sub>4</sub>

(3)  $Fe^{3+} + SCN$ 

(4) None of these

25. Which of the following nitrates are water soluble?

(1) NaNO<sub>3</sub>

(2) AgNO<sub>3</sub>

(3)  $Hg(NO_3)_2$ 

(4) LiNO<sub>3</sub>

26. Which of the following reagents can be used to distinguish between SO<sub>2</sub> and CO<sub>2</sub>?

(1) Lime water

(2) Zinc nitroprusside paste in water

(3) Potassium iodate and starch

(4) Acidified potassium dichromate solution

27. Each of these solutions is added to a mixture of aqueous solutions of iodide and chloroform (CHCl<sub>3</sub>) separately. Which will give a positive test for iodine when the solutions are vigorously mixed?

(1) NaCl solution

(2) NaBr solution

(3) Chlorine water

(4) Bromine water

28. For the lime water test, if the observations are positive for the unknown sample, then which of the following conclusion(s) is/are incorrect?

(1) Sample has only NO<sub>2</sub>

(2) Sample has only  $SO_3$ 

(3) Sample has  $CO_2$  and  $SO_2$  (4) Sample has  $H_2S$ 

29.  $CaCO_3 \longrightarrow A + B(gas)$  $A + H_2O \longrightarrow C$ 

$$C + B \longrightarrow D + H_2O$$
(White ppt.)

$$D + B(gas) \longrightarrow E \xrightarrow{Boil} BaCl_{2} F$$
(Water soluble) (White ppt.)

Select the correct option(s) for white ppt. shown in the above reactions:

(1) CaCO<sub>2</sub>

(2) MgCO<sub>2</sub>

(3) BaCO<sub>3</sub>

(4) Na<sub>2</sub>CO<sub>2</sub>

30. Which of the following statement(s) is/are correct?

(1) In  $S_2O_3^{2-}$ , both sulphur are different in nature.

(2) Sodium acetate and lead acetate on heating giving same type of product, whereas Mn, Sn, Fe oxalate salt giving different type of products.

(3) Aqueous solution of OCl<sup>©</sup>, S<sup>2-</sup> and CO<sub>3</sub><sup>2-</sup> are basic in

(4)  $\mathrm{NO_2}^{\ominus}$  oxidises  $\mathrm{I}^{\ominus}$  whereas  $\mathrm{Br_2}$  and  $\mathrm{Cl_2}$  oxidise  $\mathrm{NO_2}^{\ominus}$ .

31. Which of the following anion(s) is/are interfering radicals?

 $(1) BO_3^{3-}$ 

(2) F<sup>⊖</sup>

(3)  $PO_4^{3-}$ 

(4) None of these

#### Part-B (Analysis of Cations)

32. Blue coloured compounds are obtained when

(1) Fe<sup>2+</sup> ions react with potassium ferricyanide

(2) Fe<sup>3+</sup> ions react with potassium ferrocyanide

(3) Fe<sup>3+</sup> ions react with potassium ferricyanide

(4) Fe<sup>2+</sup> ions react with potassium ferrocyanide

33. Potassium ferrocyanide is used in the detection of

 $(1) \text{ Fe}^{2+} \text{ ions}$ 

(2)  $Fe^{3+}$  ions

 $(3) Cu^{2+} ions$ 

(4) Cd<sup>2+</sup> ions

34. Bromine is not recognised by its

(1) Ability to turn starch iodide paper blue

(2) Ability to dissolve in CS<sub>2</sub> to give an orange colour to the organic layer

(3) Ability to dissolve in CS<sub>2</sub> to give a violet colour to the organic layer

(4) Ability to turn FeSO<sub>4</sub> solution black.

35. I<sub>2</sub> can be obtained from KI solution by the action of

(1) Cl<sub>2</sub>

(2) Br<sub>2</sub>

(3) Soluble Cl<sup>⊖</sup>

(4) Soluble Br<sup>⊕</sup>

36. Which of the following is not precipitated by H<sub>2</sub>S in presence of conc. acid soln.

 $(1) Cu^{2+}$ 

 $(2) Al^{3+}$ 

 $(3) \text{ Sb}^{3+}$ 

 $(4) \text{ Cd}^{2+}$ 

37. Which of the following is (are) soluble in excess of NaOH?

 $(1) \operatorname{Cr}(OH)_3$ 

(2) Fe(OH)<sub>2</sub>

 $(3) Al(OH)_3$ 

 $(4) Zn(OH)_{2}$ 

**38.** Select the correct statement(s):

(1) When HgCl<sub>2</sub> reacts with carbonate ion, then basic mercury(II) carbonate is formed.

8.54	Inorganic Chemistry  (2) When HaCl react	s with carbonate ion, then pH of	49	. Which of the following	g metal sulphide is soluble in hot and		
	solution highly incre			dil. HNO <sub>3</sub> ?			
	• .	nate acts as buffer reacting with the		$(1) Ag_2S$	(2) PbS		
	hydrogen ions forme		2	(3) CdS	(4) HgS		
	$CO_3^{2-} + 2H^{\oplus} \longrightarrow$	$CO_2$ + $H_2O$	50	which of the following solution?	g ppt. is soluble in dil. $\mathrm{HNO_3}$ and $\mathrm{NH_3}$		
	(4) White ppt. of MgCo	O <sub>3</sub> soluble in dil. H <sub>2</sub> SO <sub>4</sub> .		(1) Ag2S2O3	$(2) Ag_2CO_3$		
39	9. Concentrated aqueous	sodium hydroxide cannot separate a		$(3) \operatorname{Ag}_{2} \operatorname{SO}_{3}$	$(4) \operatorname{AgI}$		
	mixture of		51		g ppt. is insoluble in NH <sub>3</sub> solution?		
	(1) $Al^{3+}$ and $Sn^{2+}$	(2) $AI^{3+}$ and $Fe^{3+}$	31	(1) AgI	(2) Ag2S		
	(3) $Al^{3+}$ and $Zn^{2+}$	(4) $Zn^{2+}$ and $Pb^{2+}$		(3) AgCl	(4) AgBr		
4	<b>0.</b> The metal ion(s) which	is/are not precipitated when H <sub>2</sub> S is	52	( )	ng will be completely or partially		
	passed with HCl is/are	(2) Ni <sup>2+</sup>	5-2	dissolved in NH <sub>4</sub> OH?	y partially		
	(1) $Zn^{2+}$ (3) $Cd^{2+}$	(4) $Mn^{2+}$		(1) AgCl	(2) AgBr		
	(5) Cd	of a substance gives a white		(3) BaSO <sub>4</sub>	(4) AgI		
4	1. An aqueous solution of a substance gives a white precipitatate on treatment with dil. HCl which dissolves on		53.	. Interfering radicals int			
	heating. When H <sub>2</sub> S is pa	issed through the not acidic solution,	(1) Group III radicals only				
	a black precipitate is ob	otained. The substances are not.		(2) Group III radicals			
	$(1) \operatorname{Hg_2}^{2^+} \operatorname{salt}$	(2) Cu <sup>2+</sup> salt		` '	present in group II filtrate		
	$(3)$ Ag <sup><math>\oplus</math></sup> salt	(4) Pb <sup>2+</sup> salt		(4) None of the above			
4	2. When H <sub>2</sub> S gas is passe solution of CuCl <sub>2</sub> , HgC	d through HCl containing aqueous $l_2$ , BiCl <sub>3</sub> and CoCl <sub>2</sub> , then which of	54.	ferrocyanide?	ving is/are correct for potassium		
	the following precipitat				recipitate with Cu <sup>2+</sup> ions		
	(1) CuS	(2) HgS			pitate of mixed salt with Cd <sup>2+</sup> ions		
	$(3) \operatorname{Bi}_2 S_3$	(4) CoS			white precipitate with Zn <sup>2+</sup>		
43		is/are soluble in excess of NaOH?		근 없다는 사람들이 얼마가 그 말에 그렇게 되었다.	red colouration with Fe <sup>3+</sup>		
	$(X)$ : $Pb(OH)_2(Y)$ : $CuS$		55.		g statements is not correct?		
	(1) X	(2) Y			s soluble in hot water and reappears		
	(3) Z	(4) None of these		on cooling	solubility of PbCl <sub>2</sub> is higher than the		
44.		ns $Zn(CH_3COO)_2$ , $Cd(CH_3COO)_2$ On passing $H_2S$ gas, there is a		hot water	-		
	precipitation of	-		(3) In concentrated HC	_		
	$(1) Zn^{2+}$	(2) $Cd^{2+}$	<b>.</b>		forms the complex with conc. HCl		
	$(3) Cu^{2+}$	(4) None of these	56.		g compounds are having white ppt.?		
45.		pairs can be separated by H <sub>2</sub> S in		(1) $K_2$ Fe[Fe(CN) <sub>6</sub> ]	(2) $[Fe(H_2O)_5(SCN)]^{2^+}$		
	dil HCl2			(3) ZnS	$(4) Zn(OH)_2$		

dil. HCl?

(1) Cu<sup>2+</sup> and Cd<sup>2+</sup>

(2) Cu<sup>2+</sup> and Ni<sup>2+</sup>

(3)  $Cu^{2+}$  and  $Zn^{2+}$ 

(4)  $Hg^{2+}$  and  $Al^{3+}$ 

46. An inorganic salt solution on treatment with HCl will not give a white precipitate of which metal ions?

 $(1) \text{Hg}_2^{2+}$ 

 $(2) Hg^{2+}$ 

(3)  $Zn^{2+}$ 

 $(4) A1^{3+}$ 

47. Ammonium molybdate is used to test the radical:

(1)  $PO_4^{3-}$ 

 $(2) \text{ AsO}_{4}^{3-}$ 

(3)  $Cu^{2+}$ 

(4) Ag<sup>⊕</sup>

48. Which of the following chlorides are water soluble?

(1) AgCl

 $(2) Hg_2Cl_2$ 

(3) HgCl<sub>2</sub>

(4) NaCl

 $(2) Cu^{2+}$ (1)  $Ni^{2+}$ (4) Mn<sup>2+</sup>

 $(3) \text{ Co}^{2+}$ 

in the form of ppt.?

 $(1) \operatorname{Bi}_2 S_3$ 

(3) CdS

precipitation:

59. Which of the following sulphides are soluble only in aqua regia?

57. Which of the following compounds do not have white colour

58. Out of Cu<sup>2+</sup>, Ni<sup>2+</sup>, Co<sup>2+</sup> and Mn<sup>2+</sup>, of those that dissolve

in dil. HC1, only one gives a precipitate when H<sub>2</sub>S is passed. Identify the corresponding order which do not give

(1) NiS

(2) CoS

(2)  $Co[Hg(SCN)_4]$ 

(4) Bil<sub>3</sub>

(4) CdS (3) HgS

 $\chi$  + dil. HCl  $\longrightarrow$ (White turbidity) (ion) Reagent

White ppt.  $\frac{\text{Heat}}{\text{aq. suspension}}$  Black ppt.

Which of the following cation may be present in white ppt?

- $(1) Pb^{2+}$
- $(2) \text{ Hg}^{2+}$
- (3) Ag<sup>⊕</sup>
- (4)  $Bi^{3+}$

1. Which of the following is/are correct process for the separation of given ions?

(1) Cu<sup>2+</sup> from the mixture of Cu<sup>2+</sup> and Cd<sup>2+</sup> in aqueous solution,

$$Cu^{2^{+}} + Cd^{2^{+}} \xrightarrow{Add \text{ excess}} \xrightarrow{RCN} \xrightarrow{Pass H_2S} Cu^{2^{+}} \text{ in the filtrate.}$$

(2)  $Cu^{2+}$  from the mixture of  $Cu^{2+}$  and  $Cd^{2+}$  in aqueous

$$Cu^{2^{+}} + Cd^{2^{+}} \xrightarrow{Add \text{ excess}} \xrightarrow{Pass H_2 S} Cu^{2^{+}} \text{ in the precipitate}$$

(3)  $Zn^{2+}$  from the mixture of  $Zn^{2+}$  and  $Cu^{2+}$  in aqueous solution.

$$Zn^{2+} + Cu^{2+} \xrightarrow{H_2S + dil \ HCl} \xrightarrow{Filter} Zn^{2+}$$
 in the precipitate.

(4) Fe<sup>3+</sup> from the mixture of Fe<sup>2+</sup> and Fe<sup>3+</sup> in aqueous solution.

$$Fe^{2+} + Fe^{3+} \xrightarrow{\text{solution and filter}} Fe^{3+}$$
 in the precipitate.

## Part-C (Dry Test)

- 62. Flame test is not given by
  - $(1) \text{ Mg}^{2+} \text{ ions}$
- (2) Ba<sup>2+</sup> ions
- (3) Be<sup>2+</sup> ions
- (4)  $Ca^{2+}$  ions
- 63. Borax bead test test is not given by
  - (1) Copper salts
- (2) Nickel salts
- (3) Aluminium salts
- (4) Magnesium salts
- 64. Which of the following respond to borax bead test?
  - (1) Nickel salts
- (2) Copper salts
- (3) Cobalt salts
- (4) Aluminium salts
- 65. In broax bead test, which compound(s) is/are not formed?
  - (1) Orthoborate
- (2) Metaborate
- (3) Double oxide
- (4) Tetraborate
- 66. Which of the following cation(s) will turn blue in oxidising flame?
  - $(1) \text{ Co}^{2+}$
- (2)  $Cr^{3+}$
- (3)  $Ni^{2+}$

- (4) Cu<sup>2+</sup>
- 67. Which of the following substances are green?
  - (1)  $Fe(BO_2)_3$
- (2) Cu
- (3)  $Cr(BO_2)_3$
- (4)  $Co(BO_2)_2$
- 68. Borax bead test is given by
  - (1)  $Co^{2+}$
- (2) Zn<sup>2+</sup>
- $(3) Cu^{2+}$
- $(4) Ni^{2+}$

- **69.** Colourless salt (X)  $\xrightarrow{\Delta}$  (Y)  $\xrightarrow{Cu^{2+}, \Delta}$  coloured bead (Z) (X) can be
  - (1) Borax
- (2) Microcosmic salt
- (3) Copper sulphate
- (4) None of these

#### Part-D (Miscellaneous)

- 70. Select the correct statement(s):
  - (1) Normal and polysulphides of alkali metals are soluble in water.
  - (2) The sulphides of aluminium, chromium and magnesium can only be prepared under dry conditions as they are completely hydrolysed by water.
  - (3) When filter paper is moistened with a solution of sodium nitroprusside made alkaline with sodium hydroxide or ammonia solution, a purple colouration is produced with free hydrogen sulphide.
  - (4) Thiosulphate salts of Pb, Ag and Ba are insoluble and dissolve in excess of sodium thiosulphate solution forming thiosulphate.

71. 
$$A \xrightarrow{\text{Cold} \\ \text{BaCl}_2} \text{White} \xrightarrow{\text{Filtered}} \text{Filtrate} \xrightarrow{\text{H}_2\text{O}_2} \text{Blue litmu}$$
two anions)

Blue litmu
turns red

Mixture of A contains:

- (1)  $\mathrm{CO_3}^{2-}$ ,  $\mathrm{HCO_3}^{\ominus}$  anions (2)  $\mathrm{CO_3}^{2-}$ ,  $\mathrm{HSO_3}^{\ominus}$  anions
- (3)  $SO_3^{2-}$ ,  $HSO_3^{\Theta}$  anions (4) None of these
- 72. Which of the following statement(s) is/are incorrect?
  - (1) Manganese salts give a violet borax bead test in reducing
  - (2) From a mixed precipitate of AgCl and AgI, ammonia solution dissolves only AgCl.
  - (3) Ferric ions give a deep green precipitate on adding potasssium ferrocyanide solution.
  - (4) On boiling the solution having  $K^{\oplus}$ ,  $Ca^{2+}$  and  $HCO_3^{\ominus}$ ions, we get a precipitate of K<sub>2</sub>Ca(CO<sub>3</sub>)<sub>2</sub>.
  - 73. A solution of colourless salt H on boiling with excess NaOH produces a non-flammable gas. The gas evolution ceases after sometime. Upon addition of Zn dust to the same solution, the gas evolution restarts. The colourless salt(s) H is (are)
    - $(1) NH_4NO_3$
- $(2) NH_{1}NO_{2}$
- (3) NH<sub>4</sub>Cl
- $(4) (NH_4)_5 SO_4$
- 74. Which of the following statements is/are not true?
  - (1) Fe<sup>2+</sup> (aq) gives brown colour with NH<sub>4</sub>SCN.
  - (2) Fe<sup>3+</sup> (aq) gives blood-red colour with NH<sub>4</sub>SCN.
    (3) Fe<sup>2+</sup> (ap) Vields open
  - $_{(aq)}$  yields orange colour with  $K_3$ Fe(CN)<sub>6</sub>. (4) Ag<sup>⊕</sup> reacts with CO<sub>3</sub><sup>2-</sup> then black ppt. is formed.
- 75. Which of the following react with dil. H<sub>2</sub>SO<sub>4</sub>?
  - $(1) CaCO_3$
- (2) KNO<sub>2</sub>
- (3) Na<sub>2</sub>S
- (4) BaCl<sub>2</sub>

- **76.** Conc. H<sub>2</sub>SO<sub>4</sub> will not give any gas with:
  - $(1) ZnSO_4$
- (2) barium phosphate
- (3) magnesium borate
- (4) sodium oxalate
- 77. Select the correct statement(s):
  - (1) All carbonate salts are soluble except carbonate salts of alkali metals and (NH<sub>4</sub>)<sub>2</sub>CO<sub>3</sub>.
  - (2) All bicarbonate salts are soluble except NaHCO<sub>3</sub> which is sparingly soluble.
  - (3) All sulphite salts are insoluble except sulphite salts of alkali metals and (NH<sub>4</sub>)<sub>2</sub>SO<sub>3</sub>.
  - (4) All  $MnO_4^{\ \ \ }$  salts are insoluble.
- **78.** Select the correct statement(s):
  - (1) White ppt. of BaCO<sub>3</sub> and CaCO<sub>3</sub> is soluble in dil. HNO<sub>3</sub>, dil HCl, CH<sub>3</sub>COOH and soda water.
  - (2) White ppt. of PbCO<sub>3</sub> is soluble in dil. HNO<sub>3</sub>, dil. HCl, excess of NaOH and CH<sub>3</sub>COOH.
  - (3) White ppt. of Ag<sub>2</sub>CO<sub>3</sub> is soluble in dil. HNO<sub>3</sub> and NH<sub>3</sub> solution.
  - (4) HCN and  $H_3BO_3$  are stronger acids than  $H_2CO_3$ .
- **79.** Select the correct statement(s):
  - (1) HCl is not used as acid for titration of SO<sub>2</sub>.
  - (2) Soda extract solution is very useful when any insoluble salt is present in a given mixture.
  - (3) SO<sub>2</sub> gas is identified by a filter paper moistened with potassium iodate and starch solution.
  - (4) When zinc and sulphuric acid react with sulphite, then hydrogen sulphide gas is evolved which may be detected by holding lead acetate paper to the mouth of the test tube.
- **80.** Select the correct statement(s):
  - (1)  $Ag_2S_2O_3$  appears as white precipitate when  $Na_2S_2O_3$  reacts with  $AgNO_3$ .
  - (2) Ag<sub>2</sub>S<sub>2</sub>O<sub>3</sub> is unstable turning black on standing due to formation of Ag<sub>2</sub>S.
  - (3)  $S_2O_3^{2-}$  can form soluble complex  $[Ag(S_2O_3)_2]^{3-}$  with  $Ag^{\oplus}$ .
  - (4) Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> is used in photography.
- **81.** Which of the following complex(s) will have blue colour solution or ppt.?
  - (1)  $[Cu(NH_3)_4]SO_4$
- (2)  $[Cu(NH_3)_4]$  (OH)<sub>2</sub>
- (3)  $Co[Hg(SCN)_4]$
- (4)  $K_3[Co(NO_2)_6]$
- **82.** Which of the following statement(s) is(are) true?
  - (1) Soluble bicarbonates give white precipitate with MgCl<sub>2</sub> in cold
  - (2) Soluble calcium bicarbonates give white precipitate with dilute ammonia solution followed by MgSO<sub>4</sub>.
  - (3) Bicarbonates are generally soluble in water.
  - (4) Hg(II) chloride forms a reddish-brown precipitate in a solution of soluble carbonate.
- 83. Which of the following statement(s) is(are) correct?
  - (1) Soluble sulphide gives black precipitate with AgNO<sub>3</sub> solution which is soluble in hot dilute nitric acid.

- (2) Soluble sulphide produces a yellow precipitate with a suspension of cadmium carbonate.
- (3) Sulphide ion reacts with sodium nitroprusside and gives a purple colouration.
- (4) Free H<sub>2</sub>S gas forms white precipitate with tetrahydroxido plumbate(II) solution.
- 84. Which of the following statement(s) is(are) incorrect?
  - (1) In thiourea test for nitrite, a green coloured solution is obtained.
  - (2) It is not necessary to carry out the chromyl chloride test in a dry test tube.
  - (3) In PbNO<sub>3</sub>, the brown ring test can be performed with its
  - (4) Suspension of CdCO<sub>3</sub> gives black ppt. with sodium sulphide solution.
- 85. Which of the following is(are) correct?
  - (1)  $[Al(OH)_4]^{\Theta} + NH_4^{\Theta} \xrightarrow{(aq)} \xrightarrow{Slightly heat}$  white precipitate and liberation of ammonia
  - (2)  $Pb^{2+}_{(aq)} + 2Br^{\Theta}_{(aq)} \longrightarrow Red precipitate$
  - (3) BiI<sub>3</sub> (black precipitate) + H<sub>2</sub>O(l)  $\xrightarrow{\Delta}$  Orange turbidity
  - (4)  $\operatorname{Fe}^{3+}_{(aq)} + \operatorname{K}_{4} [\operatorname{Fe}(\operatorname{CN})_{6}]_{(aq)} \longrightarrow \operatorname{Blue} \operatorname{precipitate}$
- **86.** Pick out the correct statement(s):
  - (1) Golden yellow PbI<sub>2</sub> dissolves in hot water to give a colourless solution.
  - (2) Ba<sup>2+</sup> and Ca<sup>2+</sup> ions can be separated by adding SO<sub>4</sub><sup>2-</sup> ion in acetic acid medium.
  - (3) Salts of calcium, copper and nickel give a green flame colour.
  - (4) The sulphide ion gives with alkaline sodium nitroprusside, a violet colour.
- **87.** Which of the following statement(s) is(are) true?
  - (1) Cu<sup>2+</sup> salts form soluble complex with excess KCN.
  - (2)  $Cu^{2+}$  salts form soluble complex with aqueous ammonia.
  - (3)  $Cu^{2+}$  salts form soluble complex with KI.
  - (4) A piece of iron or zinc when placed in Cu<sup>2+</sup> salt solution, precipitates copper.
- **88.** Which of the following statement(s) is/are true?
  - (1) In a mixture of Sr<sup>2+</sup> and Ca<sup>2+</sup>, ammonium sulphate precipitates only Sr<sup>2+</sup> as SrSO<sub>4</sub> but CaSO<sub>4</sub> dissolves in ammonium sulphate forming a soluble complex.
  - (2) Barium chromate is insoluble in dilute acetic acid.
  - (3) Cr(OH)<sub>3</sub> is soluble in NaOH and Br<sub>2</sub> water while Fe(OH)<sub>3</sub> is insoluble.
  - (4) Cu and Cd separation is based upon the fact that in presence of excess KCN, only Cd is precipitated as sulphide on passing H<sub>2</sub>S.
- 89. Potassium cyanide is used for separating
  - (1)  $Co^{2+}$  and  $Ni^{2+}$
- (2)  $Cu^{2+}$  and  $Cd^{2+}$
- (3)  $Mn^{2+}$  and  $Zn^{2+}$
- (4)  $Ba^{2+}$  and  $Ca^{2+}$

Excess of hypo soln. white ppt.

# Linked Comprehension Type

## <sub>paragraph</sub> 1

(B) (white turbidity which Colourless) redissolves in HCl)

Soln. of A H<sub>2</sub>S

(D) (g)  $\xrightarrow{\text{with Hg}_2^{2+}}$  (E) (white ppt.) (Water soluble)

- 1. Identify A.
  - (1) BiOCl
- (2) Bi<sub>2</sub>S<sub>3</sub>
- (3) BiCl<sub>2</sub>
- (4) BaSO<sub>4</sub>
- 2. Identify B.
  - (1) BiOCl
- (2) BaS
- (3) BiCl<sub>3</sub>
- (4) None of these
- 3. Identify C.
- (1) BiOCl
- $(2) Bi_{2}S_{3}$
- (3) BiCl<sub>3</sub>
- $(4) H_{2}S$
- 4. Identify D.
  - (1) Br<sub>2</sub>

(2) HCl

 $(3) I_{2}$ 

- (4) Cl<sub>2</sub>
- 5. Identify E.
  - (1)  $Hg_2(NO_3)_2$
- (2) HCl
- (3) Hg<sub>2</sub>Cl<sub>2</sub>
- (4) HNO<sub>3</sub>

## Paragraph 2

Greenish crystalline]  $\xrightarrow{\text{BaCl}_2 \text{ Soln.}}$  (B) (white ppt. insoluble compounds (A)

 $\Delta$ 

 $C_{(g)} + D_{(g)} + H_2O_{(g)} + E$  (Red brown residue) Conc. HCl, ppt. dissolves

 $G(\text{yellow} \overset{\text{H}_2S}{\longleftarrow} F(\text{yellow solution}) \xrightarrow{K_4[Fe(CN)_6]} \text{Blue ppt.}$ white ppt.) SnCl<sub>2</sub> Green soln. Filter

H(Greenish filtrate)

- 6. Identify compound A.
  - $(1) ZnSO_47H_2O$
- $(2) \text{ FeSO}_4.7\text{H}_2\text{SO}_4$
- (3) MgSO<sub>4</sub>7H<sub>2</sub>O
- (4) CuSO<sub>4</sub>.5H<sub>2</sub>O
- 7. Gases C and D are
  - $(1) SO_{2}, SO_{3}$
- (2) SO<sub>3</sub>, CO<sub>2</sub>
- (3) NO<sub>2</sub>, MgO
- (4) ZnO, SO<sub>3</sub>
- 8. Identify yellow solution F.
  - $(1) \text{ Fe}_2O_3$
- (2) FeCl<sub>3</sub>
- (3) ZnCl<sub>2</sub>
- (4) CuCl
- 9. Identify G.
  - (1) SO<sub>2</sub>

(2) ZnS

(3) S

(4) FeS

Paragraph 3

 $\xrightarrow{\text{Aq. BaCl}_2}$  A ppt. (insoluble in dil. HCl) Compound (X) Excess  $K_4[Fe(CN)_6]$ Chocolate

Brown ppt. -

coloured ppt. 10. Identify X.

- (1)  $CuSO_4$
- (2) BaSO<sub>4</sub>
- (3) BaCl<sub>2</sub>
- (4) NaI
- 11. What is the formula of chocolate coloured ppt.?
  - (1)  $Fe_{4}[Fe(CN)_{6}]$
- (2) Cu<sub>2</sub>[Fe(CN)<sub>2</sub>]
- (3)  $Cu_2[Fe(CN)_4]$
- (4) Cu(CN)<sub>2</sub>
- 12. What is the formula of brown ppt.?
  - (1) Cu<sub>2</sub>I<sub>2</sub>
- $(2) \operatorname{Cu}_2 I_2 + I_3^{\ominus}$
- (3) CuI<sub>2</sub>
- (4)  $CuSO_4$

## Paragraph 4

 $\Delta$  (B) (White anhydrous residue) Compound (A) -(Hydrated light Soluble in H<sub>2</sub>O green  $F_{(g)} + E_{(g)} + D$ (brown residue) (B) Dark brown compound  $KMnO_4/H^{\oplus}$  BaCl<sub>2</sub> White ppt.

Pink colour of KMnO<sub>4</sub> is discharged

- 13. Identify C.
  - (1)  $[Fe(H_2O)_5NO]SO_4$
- $(2) \text{Na}_{2} \text{SO}_{4}$
- (3) Na<sub>2</sub>[Fe(CN)<sub>5</sub>NO]
- $(4) \operatorname{Fe}_{1}[\operatorname{Fe}(\operatorname{CN})_{6}]_{3}$
- 14. Identify B.
  - (1) ZnSO<sub>4</sub>
- (2) CuSO<sub>4</sub>
- $(3) MgSO_4$
- (4) FeSO<sub>4</sub>
- 15. Identify D.
  - (1) ZnO
- (2) FeO
- (3)  $Fe_2O_3$
- (4) CuO

## Paragraph 5

White compound  $\xrightarrow{\text{HCl}}$  White ppt.  $\xrightarrow{\text{Cl}_2}$  Soluble (A) (C) (i) FeSO<sub>4</sub> ΚI (ii) conc. H<sub>2</sub>SO<sub>4</sub> Soluble compound  $\leftarrow \frac{\text{Excess of}}{\text{ppt.}}$ Brong ring (F)

(Used for detecting NH<sub>4</sub><sup>⊕</sup> ions)

- 16. Compound (A) is
  - (1) HgI<sub>2</sub>

- $(2) K_2 HgI_4$
- $(3) \operatorname{Hg}(NO_3)_2$
- $(4) Hg_2(NO_3)_2$
- 17. Oxidation state of Fe in compound (F) is
  - (1) + 1

(2) + 2

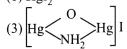
(3) + 3

- (4) + 4
- 18. (D)  $+ (NH_4)_2SO_4 \longrightarrow \text{brown ppt. (G)}$ in basic medium

Hence, compound (G) is

(1) HgI<sub>2</sub>

 $(2) NH_{4}I$ 



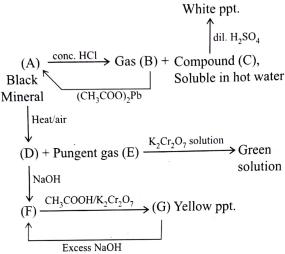
(4) Hg(NH<sub>2</sub>)I

19. White ppt. (B) + NH<sub>3</sub>  $\longrightarrow$  Black ppt. (H).

Hence, (H) is due to the formation of

- (1) Hg(NH<sub>2</sub>)Cl
- (2) Hg
- (3) Hg(NH<sub>2</sub>)Cl + Hg
- (4) Hg(NH<sub>2</sub>)

### Paragraph 6



- 20. Gas (B) on passing through CdSO<sub>4</sub> solution will give
  - (1) Black ppt.
- (2) Yellow ppt.
- (3) Orange ppt.
- (4) No ppt.
- 21. Compound (A), (B) and (E) are respectively
  - (1) CuS, H<sub>2</sub>S, SO<sub>2</sub>
- (2) PbS, H<sub>2</sub>S, SO<sub>2</sub>
- (3) PbS, H<sub>2</sub>S, SO<sub>3</sub>
- (4) ZnS, H<sub>2</sub>S, SO<sub>2</sub>
- 22. Compound (C) and (D) are respectively
  - (1) PbO, PbCl,
- (2) PbCl<sub>2</sub>, PbO
- (3) PbO, PbO,
- (4) PbS, PbO

#### Paragraph 7

i. (A) 
$$\xrightarrow{\text{NaOH}}$$
 (B) (g)  $\xrightarrow{\text{HCl}}$  White fumes.

ii. After (B) is expelled completely, resultant alkaline solution again gives gas (B) on heating with zinc.

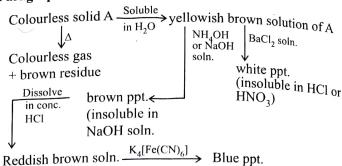
iii. (A) 
$$\xrightarrow{\Delta}$$
 N<sub>2</sub>O + H<sub>2</sub>O

- 23. Identify A.
  - $(1) NH_{\perp}NO_{2}$
- $(2) NH_{1}NO_{2}$

- (3) HC1
- $(4) \text{ Na}_2 \text{SO}_4$
- 24. Identify B.
  - (1) SO<sub>2</sub>

- (2) NH<sub>2</sub>
- $(3) N_2O$
- (4) NO<sub>2</sub>
- **25.** What is the formula of white fumes?
  - $(1) NH_4NO_3$
- $(2) NH_{1}C1$
- $(3) NH_4NO_2$
- (4) NH<sub>3</sub>

#### Paragraph 8



- 26. Identify A.
  - $(1) \text{ FeSO}_4$
- $(2) \text{ Fe}_{2}(SO_{4})_{2}$
- $(3) \text{ Fe}_{2}O_{3}$
- (4) FeO
- 27. What is the formula of brown ppt?
  - $(1) \text{ Fe}(OH)_3$
- $(2) \operatorname{Fe}(OH)_2$ (4) None of these
- (3) FeCl<sub>3</sub> 28. Which of the following complex is formed when A reacts

(2) Turnbull's blue

(1) Prussian blue (3) Brown ring complex

with  $K_4[Fe(CN)_6]$ ?

(4) Sodium nitroprusside

#### Paragraph 9

Solid (A)

(White, water insoluble)

HCl or excess of NaOH

Clear soln. (B) 
$$\xrightarrow{H_2S}$$
 No reaction

Neutralise and pass  $H_2S$ 

white ppt. (D)

- 29. Identify A.
  - (1) ZnS

(2) ZnO

- (3) MgO
- (4) FeO
- 30. Identify B.
  - (1) FeCl<sub>2</sub>
- (2) NiCl<sub>2</sub>
- (3) ZnCl<sub>2</sub>
- (4) FeCl<sub>3</sub>
- 31. Identify C.
  - (1) Na<sub>2</sub>ZnO<sub>2</sub>
- $(2) Zn(OH)_{2}$
- $(3) \text{ Fe}(OH)_3$
- (4) Fe(OH),
- 32. Identify D.
  - (1) ZnO

(2) ZnS

- (3) FeO
- (4) FeS

#### Paragraph 10

Aqueous green soln. of (A) 
$$\xrightarrow{NH_4OH}$$
 Greenish ppt. (B)

Bright yellow  $\xleftarrow{Aq. Pb(NO_3)_2}_{+ Base}$  Orange  $\xleftarrow{Acidify}_{soln. (C)}$  yellow soln. (C)

- 33. Identify A.
  - (1) AlCl<sub>3</sub>
- $(2) Cr(OH)_3$
- (3) CrCl<sub>2</sub>
- (4) None of these

(3) Mn(OH),

(4) CrO<sub>4</sub>2-

35. Identify C.

(1) Na<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>

 $(2) Na_2CrO_4$ 

(3) Na<sub>2</sub>MnO<sub>4</sub>

(4) NaMnO<sub>4</sub>

36. Identify D.

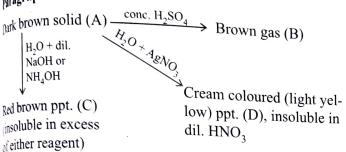
(1) PbS

(2) PbI<sub>2</sub>

(3) PbCrO<sub>4</sub>

 $(4) \operatorname{Zn(OH)}_2$ 

## <sub>paragr</sub>aph 11



of either reagent) 37. Identify A.

insoluble in excess

(1)  $Fe(NO_2)_3$ 

(2) ZnBr<sub>2</sub>

(3) FeBr<sub>3</sub>

(4) ZnCl<sub>2</sub>

38. Identify B.

(1) Cl<sub>2</sub>

(2) Br<sub>2</sub>

(3) NO<sub>2</sub>

 $(4) I_{2}$ 

39. Identify C.

 $(1) \text{ Fe}(OH)_3$ 

 $(2) \operatorname{Fe}_{2} O_{3}$ 

(3) FeO

(4) FeS

40. Identify D.

(1) AgCl

(2) AgF

(3) AgBr

(4) None of these

#### Paragraph 12

i. (A)  $\xrightarrow{\Delta}$  glassy transparent bead (B) on platinum wire.

(B) +  $CuSO_4 \longrightarrow coloured bead (C)$ .

ii. (A) + conc.  $H_2SO_4 + CH_3CH_2OH \xrightarrow{ignite}$  green flame (D)

iii. Aqueous solution (A) is alkaline.

41. Identify A.

(1) NaNH<sub>4</sub> HPO<sub>4</sub>·4H<sub>2</sub>O

(2)  $Na_2 B_4 O_7 \cdot 10 H_2 O$ 

(3)  $CuSO_4 \cdot 5H_2O$ 

(4) None of these

**42.** What is the formula of glassy bead (B)?

(1) NaPO<sub>3</sub>

(2) NaBO<sub>2</sub>

(3)  $NaBO_2 + B_2O_3$ 

(4) None of these

43. Identify C.

(1)  $Cu_3(PO_4)_2$ 

 $(2) CuSO_4$ 

(3)  $Cu(BO_2)_2$ 

(4) None of these

44. Identify D.

 $(1) (CH_3)_3 BO_3$ 

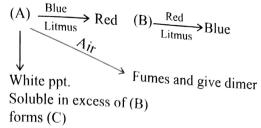
 $(2)(C_2H_5)_3BO_3$ 

(3) H<sub>3</sub>BO<sub>3</sub>

(4) None of these

## Paragraph 13

A colourless mixture of two salts (A) and (B) [excess] is soluble



45. Identify A.

(1) AlCl<sub>2</sub>

(2) ZnCl<sub>2</sub>

(3) FeCl<sub>2</sub>

(4) None of these

46. Identify B.

 $(1) Al(OH)_3$ 

 $(2) Zn(OH)_2$ 

(3) NaOH

(4) None of these

47. Identify C.

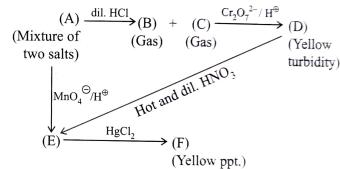
(1) Na<sub>2</sub>ZnO<sub>2</sub>

(2) NaAlO<sub>2</sub>

(3) Na<sub>2</sub>SnO<sub>2</sub>

(4) None of these

## Paragraph 14



**48.** Find the anion(s).

 $(1) SO_3^{2-}$ 

 $(2) SO_3^{2-}, S^{2-}$ 

 $(3) SO_3^{2-}, CO_2^{2-}$ 

 $(4) S_2 O_2^{2-}$ 

**49.** Find out (E).

 $(1) S^{2}$ 

 $(2) CO_3^{2-}$  $(4) SO_{1}^{2-}$ 

 $(3) S_2 O_3^{2-}$ **50.** Find out (F).

(1) HgSO<sub>4</sub>·2HgO

(2) HgSO<sub>4</sub>·3HgO

(3) HgSO<sub>4</sub>

(4) Hg,SO<sub>4</sub>·3HgO

## Paragraph 15

Cations are classified into various groups on the basis of their behaviour against some reagents. The group reagents used for the classification of most common cations are HCl, H<sub>2</sub>S, NH<sub>4</sub>OH, (NH<sub>4</sub>)<sub>2</sub>CO<sub>3</sub>. Classification is based on whether a cation reacts with these reagents by the formation of precipitates or not.

51. Which one among the following pairs of ions cannot be separated by  $H_2S$  in the presence of dilute hydrochloric acid?

(1)  $\mathrm{Bi}^{3+}$ ,  $\mathrm{Cd}^{2+}$ 

 $(2) Al^{3+}, Hg^{2+}$ 

(3)  $Zn^{3+}$ ,  $Cu^{2+}$ 

(4) Ni<sup>2+</sup>, Cu<sup>2+</sup>

**52.** An aqueous solution contains  $Hg^{2+}$ ,  $Hg_2^{2+}$ ,  $Pb^{2+}$  and  $Cd^{2+}$ . The addition of 2M HCl will precipitate:

#### Inorganic Chemistry

(1) HgCl<sub>2</sub> only

(2) PbCl<sub>2</sub> only

(3) PbCl, and Hg,Cl,

(4) PbCl<sub>2</sub> and CdCl<sub>2</sub>

53. An aqueous solution which is slightly acidic contains cations Fe<sup>3+</sup>, Zn<sup>2+</sup> and Cu<sup>2+</sup>. The reagent when added in excess to this solution would identify the separate Fe<sup>3+</sup> ion in one step

(1) 2M HCl

(2) 6M NH<sub>2</sub>

(3) 6M NaOH

(4) H<sub>2</sub>S gas

#### Paragraph 16

The reagents like AgNO<sub>3</sub>, K<sub>4</sub>[Fe(CN)<sub>6</sub>], KCNS, KI, K<sub>2</sub>CrO<sub>4</sub> Nessler's reagent, etc., find extensive and very important application in qualitative analysis because these reagents form different types of products with different cations. For example, KI forms yellow precipitate with Pb<sup>2+</sup> but it forms red precipitate with Hg<sup>2+</sup>. Hence, these reagents are widely used in the qualitative analysis of inorganic salts.

**54.** Which of the following is not correctly matched?

(1) 
$$Ag^{\oplus} + S_2O_3^{2-} \longrightarrow White$$

(1) 
$$Ag^{\oplus} + S_2O_3^{2-} \longrightarrow White ppt.$$
  
(2)  $Pb^{2+}_{(aq)} + 2Cl^{\ominus}_{(aq)} \longrightarrow Black precipitate$ 

(3) BiI<sub>3</sub> (Black precipitate) + H<sub>2</sub>O(l)  $\xrightarrow{\Delta}$  Orange turbidity.

(4) 
$$\operatorname{Ca}^{2+}_{(aq)} + \operatorname{K}_{4} [\operatorname{Fe}(\operatorname{CN})_{6}]_{(aq)} \longrightarrow \operatorname{White precipitate}$$

55. Which of the following cations (i.e., basic radicals) forms coloured (not white) precipitates with aqueous solution of potassium iodide but precipitate does not dissolve in excess of reagent?

 $(1) \text{ Hg}^{2+}$ 

(3)  $Bi^{3+}$ 

56. Which of the following hydroxide does not dissolve in ammonia solution but dissolves in sodium hydroxide?

 $(1) Zn(OH)_2$ 

 $(2) Cd(OH)_{2}$ 

 $(3) Cu(OH)_2$ 

 $(4) Al(OH)_3$ 

## Paragraph 17

#### More than one correct

NH3 solution was added to four sample solution in different test tube and found the following observation about the precipitate.

- (a) White ppt. which is soluble in excess of NH<sub>3</sub> solution.
- (b) On heating white ppt. obtained from (a) produces a compound which is white in cold but yellow on heating.
- (c) The cation present in (b) forms white ppt. with hypo solution which gives black ppt. on heating.
- (d) The cation present in (c) forms soluble complex with excess of NH<sub>3</sub> solution.

57. White ppts. in (a), (b) and (c), respectively, obtained are

- (1)  $Zn(OH)_2$ ,  $Zn(OH)_2$ ,  $HgO \cdot Hg(NH_2)NO_2$
- $(2) \operatorname{Cd}(OH)_2$ ,  $\operatorname{Zn}(OH)_2$ ,  $\operatorname{HgO-Hg}(NH_2)\operatorname{NO}_3$
- $(3) \operatorname{HgO-Hg}(\operatorname{NH}_2)\operatorname{NO}_3, \operatorname{Zn}(\operatorname{OH})_2, \operatorname{Cd}(\operatorname{OH})_2$
- $(4) Al(OH)_3$ ,  $Zn(OH)_2$ ,  $Pb(OH)_2$
- **58.** The solution initially present in (a) +  $H_2S$  (basic medium) gives ppt., then (a) may have

(1)  $Zn^{2+}$ 

 $(2) \text{ Cd}^{2+}$ 

 $(3) \text{ Co}^{2+}$ 

(4)  $Ni^{2+}$ 

59. White ppt. in (c) and the soluble complex formed from white ppt. with the hypo solution is/are

(1)  $Pb(OH)_2$ ,

 $[Pb(S_2O_3)_2]^{2-}$ 

 $(2) Ag_2O_2$ 

 $[Ag(S_2O_3)_2]^{2}$ 

(3)  $HgO \cdot Hg(NH_2)NO_3$ ,

 $[Hg(S_2O_3)_2]^{2-}$ 

(4) None of these

#### Paragraph 18

(A) is a colourless solid; it melts when heated and gives off a gas (B) which is supporter of combustion. If heating is continued, the whole of the solid disappears. When (A) is heated with an aqueous NaOH solution, an alkaline gas (C) is evolved. When gas (B) is heated with sodamine, a colourless solid (D) is formed. When (D) is heated with dil. H<sub>2</sub>SO<sub>4</sub>, a colourless liquid (F) is formed.

**60.** The compound E has

(1) Linear structure

(2) Bent structure

(3) Tetrahedral structure

(4) None of these

**61.** The name of compound E is

(1) Ammonia

(2) Hydrazoic acid (4) None of these

(3) Hydrogen amide

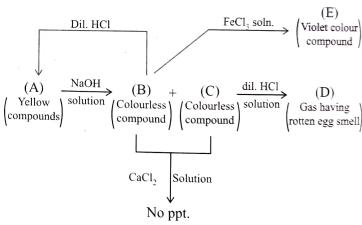
**62.** The compound C has (1) Linear geometry

(2) Pyramidal

(3) Tetrahedral

(4) None of these

#### Paragraph 19



63. Compound (B) on strong heating produces compound(s) which has/have

(1) Chain structure

(2) Tetrahedral structure

(3) Both (a) and (b)

(4) None of these

**64.** Which of the following statements is/are correct for gas (D)?

I. It has the state of hybridisation sp<sup>3</sup>.

II. Gas can be identified by CaCl<sub>2</sub> solution.

III. Gas can be identified by Pb(OAc)<sub>2</sub> solution.

IV. Gas can be identified by passing through sodium nitroprusside solution.

(1) I, IV

(2) I, III

(3) III only

(4) I, II, IV

Compound (B) on reaction with [Ni(en)<sub>3</sub>](NO<sub>3</sub>)<sub>2</sub> gives a coloured complex exhibiting

- (1) Optical isomerism
- (2) Geometrical isomerism
- (3) Linkage isomerism
- (4) No isomerism

# pragraph 20

produces solid (A) when placed into water produces a heavy turbidity of (B). Solid (A) gives a clear solution in conc. HCl. HCl solution is added to large amounts of water, (B) forms (B) dissolves in dilute HCl. When  $H_2S$  is passed through suspension of (A) or (B), a black precipitate (C) forms, (C) is polible in yellow ammonium sulphide (NH<sub>4</sub>)<sub>2</sub>S. Conc. H<sub>2</sub>SO<sub>4</sub> ided to solid (A) liberates gas (D). Gas (D) is water-soluble and white precipitate with mercuric salts (E) and not mercuric The black precipitate (C) dissolves in HNO<sub>3</sub> (1: 1) to give a abilition to which H<sub>2</sub>SO<sub>4</sub> is added followed by addition of NH<sub>4</sub>OH white precipitate (F) is formed. (E) gives a black ppt. (G) aith solution of sodium stannite.

- 66. When compound (E) reacts with NH<sub>4</sub>OH, then product is a
  - (1) White ppt.
- (2) Black ppt.
- (3) Yellow ppt.
- (4) Green ppt.
- 67. Compound (C) is also formed by the following reaction:

(1) 
$$Ba^{2+} + S_2O_3^{2-} \longrightarrow E$$
 (2)  $Bi^{3+} + S_2O_3^{2-} \longrightarrow E$ 

(2) 
$$Bi^{3+} + S_2O_3^{2-} \longrightarrow E$$

- (3)  $Bi_2S_2O_3 \xrightarrow{\Delta} E$
- (4) None of these
- 68. Compound (B) is not soluble in
  - (1) Tartaric acid
- (2) HC1
- (3) HNO<sub>3</sub>
- (4) H<sub>2</sub>SO<sub>4</sub>

## Matrix Match Type



#### 1. Match the column:

1	Column I		Column II
a.	$Fe^{3+} + SO_2 \longrightarrow$	p.	White ppt.
b.	$Pb^{2+} + Na_2S \longrightarrow$	q.	Black ppt.
c.	$SO_3^{2-} + Pb(NO_3)_2 \longrightarrow$	r.	Yellow ppt.
d.	$PbSO_3 + O_2 \xrightarrow{Boil}$	s.	Green colouration
e.	$Cd^{2+} + Na_2S \longrightarrow$		

## 2. Match the colour of precipitates listed in column (I) with the reagent(s) listed in column (II):

Column I		Column II		
a.	Bi <sup>3+</sup> gives black precipitate with	p.	Saturated solution of H <sub>2</sub> S in water	
b.	Cu <sup>2+</sup> gives black precipitate with	q.	Potassium thiocyanate solution	
c.	Zn <sup>2+</sup> gives white precipitate with	r.	Potassium iodide solution	
d.	Ag <sup>®</sup> gives white precipitate with	s.	Potassium ferrocyanide solution	

## 3. Match the column:

	Column I		Column II
a.	Fe <sup>2+</sup> reacts with K <sub>3</sub> [Fe(CN) <sub>6</sub> ]	p.	Cherryred ppt.
b.	Fe <sup>3+</sup> reacts with K <sub>4</sub> [Fe(CN) <sub>6</sub> ]	q.	Turnbull's blue
:.	Ni <sup>2+</sup> reacts with DMG	r.	Prussian blue
d.	Cu <sup>2+</sup> reacts with NH <sub>3</sub> solution	s.	Blue solution

#### 4. Match the column:

	Column I		Column II
a.	$Na_2S + Hg(NO_3)_2 \longrightarrow$	p.	Pale green solution
b.	$ \begin{array}{c} Na_2S + \\ Na_2[Fe(CN)_5NO] \\ \longrightarrow \end{array} $	q.	Black ppt.
c.	$Na_2S_2O_3 + BaCl_2 \longrightarrow$	r.	Finally purple colour
d.	$Na_2S_2O_3 + Pb(NO_3)_2$ $\longrightarrow$	s.	White ppt.
e.	$Fe^{3+} + S_2O_3^{2-} \longrightarrow$		

#### 5. Match the column:

	Column I		Column II
a.	K <sub>4</sub> [Fe(CN) <sub>6</sub> ]	p.	Produces deep blue solution with CuSO <sub>4</sub> solution
b.	(NH <sub>4</sub> ) <sub>2</sub> S	q.	Produces deep blue ppt. with FeSO <sub>4</sub> solution
c.	NH <sub>4</sub> OH (excess)	r.	Produces deep blue ppt. with FeCl <sub>3</sub> solution
d.	NaOH (excess)	S.	Produces colourless solution or white ppt. with ZnSO <sub>4</sub> solution
-/-		t.	Produces chocolate brown ppt. with CuSO <sub>4</sub> solution.

### 6. Match the substances given in column II based on reactions given in column I and select correct answer from the alternate:

	Column I		Column II
a.	A white, waxy solid, normally stored under water because it spontaneously inflames in air	p.	HNO <sub>3</sub>
b.	A viscous liquid that reacts with BaCl <sub>2</sub> , giving a white ppt.	q.	Cl <sub>2</sub>
c.	An acid that reacts with copper metal, releasing brown fumes	r.	P
d.	A pale greenish yellow gas that dissolves in aqueous NaOH to give a solution used as a bleach	s.	H <sub>2</sub> SO <sub>4</sub>

7. Match the salts listed in column (I) with the colour of the precipitate and reagent(s) listed in column (II):

Column I			Column II		
a.	FeSO <sub>4</sub>	p.	Brown precipitate with NaOH		
b.	Bi(NO <sub>3</sub> ) <sub>3</sub>	q.	White precipitate with Pb(NO <sub>3</sub> ) <sub>2</sub>		
c.	AgNO <sub>3</sub>	r.	Yellow precipitate with NH <sub>4</sub> NO <sub>2</sub> and CH <sub>3</sub> COOH on warming		
d.	CoCl <sub>2</sub>	s.	Black precipitate with H <sub>2</sub> S		

8. Match the column:

	Column I		Column II
a.	$ 3Fe^{3+} + 6 CH_3COO^{\Theta} $ Boil	p.	White ppt.
b.	$S_2O_3^{2-}+[Ni(en)_3](NO_3)_2 \longrightarrow$	q.	Blood-red colour
c.	$Fe^{3+} + \stackrel{\Theta}{SCN} \longrightarrow$	r.	Violet ppt.
d.	$CH_3COO^{\Theta} + AgNO_3 \longrightarrow$	s.	Brownish red ppt.

9. Match the column:

	Column I		Column II
a.	$NH_3 + NaOCl \xrightarrow{\Delta}$	p.	N <sub>2</sub> O
b.	$NH_4NO_2 + NaOH \longrightarrow$	q.	N <sub>2</sub>
c.	$NH_4NO_3 \xrightarrow{\Delta}$	r.	NH <sub>3</sub>
d.	$(NH_4)_2Cr_2O_7 \xrightarrow{\Delta}$	s.	H <sub>2</sub> O

10. Match the column:

	Column I		Column II
a.	PbO <sub>2</sub>	p.	Soluble in excess alkali solution
b.	ZnO	q.	Form blue colour hydroxide with alkali solution
c.	HgCl <sub>2</sub>	r.	Reacts with NaOH to form coloured ppt.
d.	CuSO <sub>4</sub>	S.	Yellow on heating

11. There are certain chemical reagents which are used in the qualitative analysis of specific acid, i.e. anionic radicals. Match the reagent listed in column I with acid radicals listed in column II.

	Column I		Column II
a.	Silver nitrate solution	p.	CO <sub>3</sub> <sup>2-</sup>
b.	Barium chloride solution	q.	SO <sub>3</sub> <sup>2-</sup>
c.	Lead nitrate solution	r.	$S^{2-}$
d.	Acidified potassium permanganate solution	s.	NO <sub>2</sub> <sup><math>\Theta</math></sup>

12. Match the precipitates of the compounds listed in column I with the solvent(s) listed in column II:

3.01N	Column I		Column II
a.	Zn(OH) <sub>2</sub> precipitate dissolves in	p.	Potassium cyanide
b.	Cr(OH) <sub>3</sub> precipitate dissolves in	q.	Ammonia solution
c.	AgCl precipitate dissolves in	r.	Sodium hydroxide
d.	CuS precipitate dissolves in	S.	Sodium peroxide

13. Column (I) contains some reagents which when taken in excess produce precipitate with radical(s) given in column (II). Accordingly match column (I) with column (II):

Column I (Reagent)		Column II (Radical)		
a.	KCN <sub>(aq)</sub>	p.	Pb <sup>2+</sup>	
b.	NaOH <sub>(aq)</sub>	q.	$Ag^{\oplus}$	
c.	KI <sub>(aq)</sub>	r.	Hg <sub>2</sub> <sup>2+</sup>	
d.	K <sub>2</sub> CrO <sub>4(aq)</sub>	S.	Cu <sup>2+</sup>	

14. Match the reactions listed in column (I) with the colour of the precipitate(s) listed in column (II):

	Column I	Column II		
a.	$Cu^{2+}_{(aq)} + 2SCN^{\Theta}_{(aq)}$ Allow to stand for sometime	p.	Brown	
b.	$Pb^{2+} + CrO_4^{2-} \longrightarrow$	q.	Reddish brown ppt.	
c.	$CO_3^{2-}+4Hg^{2+}+3H_2O\longrightarrow$	r.	Yellow	
d.	$Mn^{2+}_{(aq)} + 2OH_{(aq)}^{\Theta} \longrightarrow$	s.	White	

15. Match the column:

	Column I		Column II
a.	Red vapours	p.	MnSO <sub>4</sub> + NaBiO <sub>3</sub> + conc. HNO <sub>3</sub>
b.	NaOH solution is turned yellow by the vapours	q.	CrO <sub>2</sub> Cl <sub>2</sub>
c.	Purple solution	r.	KBr heated with MnO <sub>2</sub> and conc. H <sub>2</sub> SO <sub>4</sub>
d.	A colourless solution results when the evolved gas is absorbed in an NaOH solution	S.	[Fe(CN) <sub>5</sub> NOS] <sup>4</sup>

16. Match the column:

112	Column I		Column II
a.	Blue, soluble in amyl alcohol	p.	$(NH_4)_2[Co(SCN)_4]$
b.	White	q.	ZnS
c.	Obtained in the analysis of group III B	r.	PbSO <sub>4</sub>
d.	Soluble in an ammonium acetate solution	S.	CrO <sub>5</sub>

17. Certain substances change their colour when they are hot and revert to their original colour in cold. Match the following:

Column I			Column II		
a.	Yellow when hot and white in cold again	p.	Bi <sub>2</sub> O <sub>3</sub> and SnO <sub>2</sub>		
b.	Yellowish brown in hot and yellow in cold	q.	ZnO		
c.	Black or red in hot and brown in cold	r.	PbO		
d.	Yellow in hot and yellow in cold	s.	Fe(III) oxide (Fe <sub>2</sub> O <sub>3</sub> )		

18. Sometimes the original mixture gives characteristic smell. This also serves as an information in analysing the inorganic mixture. Match the following observation.

	Column I		Column II
a.	Vinegar or acetic acid type	p.	Ammonium salts, type (NH <sub>4</sub> ) <sub>2</sub> CO <sub>3</sub>
b.	Ammonical smell	q.	Acetates
c.	Chlorine gas smell	r.	Cyanides
d.	Bitter almond type smell	S.	Hypochlorites

19. Match the following flame tests:

	Column I		Column II
a.	Bright golden yellow	p.	Na
b.	Pale violet	q.	K
c.	Deep bluish green	r.	Cu
d.	Brick red	s.	Ca
e.	Crimson red	t.	Sr
f.		u.	Ba
e.	Crimson red Pale green	+	

20. In borax bead test, the sodium metaborate (NaBO<sub>2</sub>) and boric anhydride (B<sub>2</sub>O<sub>3</sub>) present in borax react with metallic salt to form coloured metaborates. The same metal can give different coloured beads in oxidising and reducing flames, due to formation of higher metaborates in oxidising flame and lower metaborates in reducing flame. Match the following:

-	Colour of bead in oxidising flame		Inference
	Greenish when hot, blue in cold	p.	Cu
a.	Dark green in hot and cold	q.	Cr
b.	Dark green in not and con-	1.5	

c.	Deep blue	r.	Co
d.	Yellow when hot®	s.	Fe
e.	Violet in both hot and cold	t.	Mn
f.	Brown in cold	u.	Ni

21. In charcoal cavity test, the compound is mixed with Na<sub>2</sub>CO<sub>3</sub> or with fusion mixture ( $Na_2CO_3 + K_2CO_3$ ) and placed in charcoal cavity, moistened with water and heated strongly. Match the following:

	Metals	Bea	ead and Incrustation			
a.	Bi	p.	Brittle beads, yellow			
b.	Pb	q.	Soft beads, yellow which marks the paper			
c.	Sb	r.	Brittle bead, white			

22. The principle and procedure of cobalt nitrate test (or Rinmann's test) is exactly similar to that of charcoal cavity test with slight addition i.e. after adding Na2CO3 and heating, add few drops of cobalt nitrate and heat strongly. Match the following:

Obser- vation			Comp- osition		Inference		
a.	Blue residue	I.	CoO·Al <sub>2</sub> O <sub>3</sub>	p.	Al (when phosphate and borate are absent		
b.	Green residue	П.	CoO·ZnO	q.	ZnO		
c.	Pink	III.	CoO·MgO	r.	MgO		
d.	Blue residue	IV.	NaCo PO <sub>4</sub>	s.	Phosphate in absence of Al		

23. Match the following using three columns with (X) containing radicals, (Y) the reagents used and (Z) the compound formed when (X) and (Y) react.

	X		Y		Z
a.	Fe <sup>2+</sup>	I.	NH <sub>4</sub> SCN	p.	Cherry red ppt.
b.	Fe <sup>3+</sup>	II.	DMG	q.	Turnbull's blue
c.	Ni <sup>2+</sup>	III.	K <sub>4</sub> [Fe(CN) <sub>6</sub> ]	r.	Prussian blue
d.	Co <sup>2+</sup>	IV.	K <sub>3</sub> [Fe(CN) <sub>6</sub> ]	s.	Blue

24. Match the items given in Column I with that in Column II and III

Column I  Reaction of ions  with reagent		Reaction of ions Compound		Column III Colour	
b.	$Fe^{+2}$ with $[Fe(CN)_6]^{3-}$	ii.	Fe <sub>2</sub> [Fe(CN) <sub>6</sub> ] <sup>4</sup>	q.	Prussian blue
c.	$Fe^{+3}$ with $[Fe(CN)_6]^{4-}$	iii.	Fe <sub>4</sub> [Fe(CN) <sub>6</sub> ] <sub>3</sub>	r.	Brown solution
d.	$Fe^{+3}$ with $[Fe(CN)_6]^{3-}$	iv.	Fe[Fe(CN) <sub>6</sub> ] <sup>3-</sup>	s.	Turnbull's

**25.** Match the items given in Column I with that in Column II and III.

	Column I		Column II		Column III		
lons		Reagent		Colour			
a.	Zn <sup>+2</sup>	i.	[Fe(CN) <sub>6</sub> ] <sup>3-</sup>	p.	Blue colour		
b.	Co <sup>+2</sup>	ii.	SCN <sup>⊖</sup>	q.	Reddish brown ppt		

c.	Cu <sup>+2</sup>	iii.	[Fe(CN) <sub>6</sub> ] <sup>4</sup>	r.	Chocolate colour ppt
d.	Fe <sup>+3</sup>	iv.	8-Hydroxy- quinoline	s.	Bluish white colour
e.	AI <sup>+3</sup>	v.	1, 10- Phenanthroline		Blood red colour

26. Match the items given in Column I with that in Column II and III.

	Column I		Column II		Column III		
	Separation		Reagent		Inference		
a.	Mixture of Co <sup>+2</sup> and Ni <sup>2+</sup> are distinguished by	i.	Additon of KCN	p.	Gives ppt soluble in NH <sub>4</sub> OH and another ppt insoluble in NH <sub>4</sub> OH		
b.	Mixture of Br <sup>⊕</sup> and I <sup>⊕</sup> are distinguished by	ii.	Addition of [Fe(CN) <sub>6</sub> ] <sup>4-</sup>	q.	Forms complexes and on passing H <sub>2</sub> S(g). Unstable complex gives yellow ppt		
c.	Mixture of Cu <sup>2+</sup> and Cd <sup>2+</sup> are distinguished by	iii.	Layer test	r.	Gives red colour with one ions and no colour with other ion		
d.	Mixture of SO <sub>3</sub> <sup>2-</sup> and SO <sub>4</sub> <sup>2-</sup> are distinguished by	iv.	FeCl <sub>3</sub> solution	s.	First turns violet and then brown on exces of addition of Cl <sub>2</sub>		

## **Numerical Value Type**



- 1. An aqueous solution contains  $Hg^{2+}$ ,  $Hg_2^{2+}$ ,  $Pb^{2+}$  and  $Cd^{2+}$ . Out of these, how many ions will produce white precipitate with dilute HC1?
- **2.** How many compounds liberate NH<sub>3</sub> on heating from the following?

$$({\rm NH_4})_2{\rm SO_4}, ({\rm NH_4})_2{\rm CO_3}, {\rm NH_4Cl}, {\rm NH_4NO_3}, ({\rm NH_4})_2{\rm Cr_2O_7}$$

- 3. How many water molecule(s) is/are present in microcosmic salt?
- **4.** Na<sub>2</sub>SO<sub>3</sub>, NaCl, Na<sub>2</sub>C<sub>2</sub>O<sub>4</sub>, Na<sub>2</sub>HPO<sub>4</sub>, Na<sub>2</sub>CrO<sub>4</sub>, NaNO<sub>2</sub>, CH<sub>3</sub>CO<sub>2</sub>Na are separately treated with AgNO<sub>3</sub> solution. In how many cases is/are white ppt. obtained?
- 5. Find the number of compounds which have yellow colour ppt. from the given compounds:

6. Find the number of ions which are identified by dil. HCl from the following:

- 7. Find the number of reducing agents from the following:  $H_2S$ ,  $SO_3$ ,  $CrO_4^{\ 2^-}$ ,  $Fe^{2^+}$ ,  $MnO_4^{\ \Theta}$
- 8. How many water of crystallisation is(are) present in the ore carnallite?

9. 
$$BO_3^{3-} + conc. H_2SO_4 + CH_3 - CH_2 - OH \xrightarrow{ignite} (A)$$

Green flame

What is the oxidation number of central atom that is responsible for green flame in compound (A)?

- 10. Na<sub>2</sub>SO<sub>3</sub>, Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>, Na<sub>2</sub>CO<sub>3</sub>, Na<sub>2</sub>CrO<sub>4</sub> are separately treated with AgNO<sub>3</sub> solution. In how many cases is/are red ppt. obtained?
- 11. In how many of the following reactions, one of the products is obtained as a yellow precipitate?

$$Ba^{2^{+}} + CrO_{4}^{2^{-}} \longrightarrow Product$$

$$Hg^{2^{+}} + Co^{2^{+}} + SCN^{\ominus} \longrightarrow Product$$

$$NH_{4}^{\oplus} + [PtCl_{6}]^{2^{-}} \longrightarrow Product$$

$$Ag^{\oplus} + CrO_{4}^{2^{-}} \longrightarrow Product$$

$$NH_{4}^{\oplus} + [Co(NO_{2})_{6}]^{3^{-}} \longrightarrow Product$$

- 12. A solution of Hg<sup>2+</sup> ion on treatment with a solution of cobalt(II) thiocyanate gives rise to a deep blue crystalline precipitate. Then the coordination number of mercury in the deep blue coloured compound is.
- **13.** How many water molecule(s) is/are present in compound which is used in borax bead test?
- 14.  $\operatorname{Fe}_{(aq)}^{2+} + \operatorname{NO}_{3(aq)}^{\Theta} + \operatorname{H}_{2}\operatorname{SO}_{4}(\operatorname{conc.}) \longrightarrow \operatorname{Brown ring}$ The oxidation number of iron in brown ring complex is.
- **15.** In how many of the following reactions one of the products is obtained as a black precipitate?

i. 
$$Bi(OH)_3 \downarrow + [Sn(OH)_4]^{2-}_{(aq)} \longrightarrow Products$$

ii. 
$$Bi_{(aq)}^{3+} + I_{(aq)}^{\Theta}$$
 (not in excess)  $\longrightarrow$  Products

iii. 
$$Ag \oplus_{(aq)} + H_2S_{(g)} \xrightarrow{H^{\oplus}} Products$$

iv. 
$$[BiI_4]^{\bigcirc}_{(aq)} + H_2O_{(1)} \xrightarrow{Dilution}$$
 Products

## **Archives**

## JEE MAIN

## gingle Correct Answer Type

- $H_1[X] + H_2SO_4 \longrightarrow [Y]$  a colorless gas with irritating smell,  $[Y] + K_2Cr_2O_7 + H_2SO_4 \rightarrow Green solution, [X] and [Y] are$ 
  - $(1) SO_3^{2-}$  and  $SO_3$
- $(2) Cl^-$  and HCl
- (3)  $S^{2-}$  and H,S
- (4)CO $_3^{2-}$ and CO $_2$

(AIEEE 2010)

- $_{1, A \text{ salt of NaX}} \xrightarrow{\text{MgCl}_2}$  White ppt. on boiling. Thus, anion
  - (1) HCO $_3$

 $(2) NO_{3}^{-}$ 

 $(3) CO_{2}^{2}$ 

- $(4) SO_4^{2-}$
- (AIEEE 2010)
- 3, Passing H<sub>2</sub>S gas into a mixture of Mn<sup>2+</sup>, Ni<sup>2+</sup>, Cu<sup>2+</sup>, and Hg<sup>2+</sup> ions in an acidified aqueous solution precipitates
  - (1) CuS and HgS
- (2) MnS and CuS
- (3) MnS and NiS
- (4) NiS and HgS

(AIEEE 2011)

- 4. The color of light absorbed by an aqueous solution of CuSO<sub>4</sub> is
  - (1) Orange-red
- (2) Blue-green

(3) Yellow

- (4) Violet
- (AIEEE 2011)
- 5. In the cyanide extraction process of silver from argentite ore, the oxidizing and reducing agents used are
  - (1) O, and CO, respectively
  - (2) O<sub>2</sub> and Zn dust, respectively
  - (3) HNO<sub>3</sub> and Zn dust, respectively
  - (4) HNO<sub>3</sub> and CO, respectively

(AIEEE 2012)

- 6. The gas leaked from a storage tank of the Union Carbide plant in Bhopal gas tragedy was
  - (1) Ammonia
- (2) Phosgene
- (4) Methylamine
- (3) Methylisocyanate
- (JEE Main 2013)
- 7. Which of the following is the wrong statement?
  - (1) Ozone is violet-black in solid state.
  - (2) Ozone is diamagnetic gas.
  - (3) ONCl and ONO are isoelectronic

(JEE Main 2013)

(4) O<sub>3</sub> molecule is bent.

8. The hottest region of Bunsen flame shown in the figure below is:



- region 3
- region 2
- region 1

- (1) region 4
- (2) region 1
- (3) region 2
- (4) region 3

(JEE Main 2016)

- 9. Sodium salt of an organic acid 'X' produces effervescence with conc. H<sub>2</sub>SO<sub>4</sub>. 'X' reacts with the acidified aqueous CaCl, solution to give a white precipitate which decolourises acidic solution of KMnO<sub>4</sub>. 'X' is:
  - (1) C<sub>6</sub>H<sub>5</sub>COONa
- (2) HCOONa
- (3) CH<sub>3</sub>COONa
- (4)  $Na_2C_2O_4$

(JEE Main 2017)

10. An alkali is titrated against an acid with methyl orange as indicator. Which of the following is a correct combination?

	Base	Acid	End point
(1)	Strong	Strong	Pinkish red to yellow
(2)	Weak	Strong	Yellow to pinkish red
(3)	Strong	Strong	Pink to colourless
(4)	Weak	Strong	Colourless to pink
(.)			(JEE Main 2018)

### JEE ADVANCED

## **Single Correct Answer Type**

- 1. Sulphide ores are common for the metals
  - (1) Ag, Cu and Pb
- (2) Ag, Cu and Sn
- (3) Ag, Mg and Pb
- (4) Al, Cu and Pb

(JEE Advanced 2013)

- 2. Upon treatment with ammoniacal H2S the metal ion that precipitates as sulphide is
  - (1) Fe(III)
- (2) Al(III)
- (3) Mg(II)
- (4) Zn(II)

(JEE Advanced 2013)

- 3. Roasting of sulphides gives the gas X as a by product. This is a colourless gas with choking smell of burnt sulphur and causes great damage to respiratory organs as a result of acid rain. Its aqueous solution is acidic, acts as a reducing agent and its acid has never been isolated. The gas X is
  - (1) CO<sub>2</sub>

(2) SO<sub>3</sub>

(3) H<sub>2</sub>S

- (4) SO<sub>2</sub> (JEE Advanced 2013)
- 4. Identify the correct order of solubility in aqueous medium:
  - (1)  $Na_2S \ge CuS \ge ZnS$
- (2)  $Na_2S > ZnS > CuS$
- (3)  $CuS > ZnS > Na_2S$  (4)  $ZnS > Na_2S > CuS$

(JEE Advanced 2013)

- 5. Which of the following compounds is not colored yellow?
  - $(1) \operatorname{Zn}_{2}[\operatorname{Fe}(\operatorname{CN})_{6}]$
- (2)  $K_3[Co(NO_2)_6]$
- $(3) (NH_4)_3 [As (MO_3O_{10})_4]$  (4) BaCrO<sub>4</sub>

(JEE Advanced 2015)

## **Multiple Correct Answers Type**

- 1. A solution of colourless salt H on boiling with excess NaOH produces a non-flammable gas. The gas evolution ceases after sometime. Upon addition of Zn dust to the same solution, the gas evolution restarts. The colourless salt(s) H is/are
  - $(1) NH_4NO_3$
- (2) NH<sub>4</sub>NO<sub>2</sub>
- $(3) NH_4C1$
- $(4) (NH_4)_2 SO_4$

(IIT-JEE 2008)

2. For the given aqueous reaction, which of the statement(s) is(are) true?

Excess KI + 
$$\frac{\text{Dilute H}_2\text{SO}_4}{\text{VanSO}_4}$$
 brownish-yellow solution  $\text{K}_3[\text{Fe(CN)}_6]$   $\text{ZnSO}_4$  (White precipitate + brownish-yellow filtrate)

- (1) The first reaction is a redox reaction.
- (2) White precipitate is  $Zn_3[Fe(CN)_6]_2$ .
- (3) Addition of filtrate to starch solution gives blue colour.
- (4) White precipitate is soluble in NaOH solution.

(IIT-JEE 2012)

- 3. The pair(s) of ions where BOTH the ions are precipitated upon passing H<sub>2</sub>S gas in presence of dilute HCl, is(are)
  - (1)  $Ba^{2+}$ ,  $Zn^{2+}$
- (2)  $Bi^{3+}$ ,  $Fe^{3+}$
- (3)  $Cu^{2+}$ ,  $Pb^{2+}$
- (4)  $Hg^{2+}$ ,  $Bi^{3+}$

(JEE Advanced 2015)

- 4. The reagent(s) that can selectively precipitate S<sup>2-</sup> from a mixture of  $S^{2-}$  and  $SO_4^{2-}$  in aqueous solution is (are)
  - (1) CuCl<sub>2</sub>
- (2) BaCl<sub>2</sub>
- (3) Pb(OOCCH<sub>3</sub>)
- (4)  $Na_2[Fe(CN)_5NO]$

(JEE Advanced 2016)

## **Linked Comprehension Type**

#### Paragraph 1

An aqueous solution of a mixture of two inorganic salts, when treated with dilute HCl, gave a precipitate (P) and a filtrate (Q). The precipitate P was found to dissolve in hot water. The filtrate (Q) remained unchanged, when treated with H<sub>2</sub>S in a dilute mineral acid medium. However, it gave a precipitate (R) with H<sub>2</sub>S in an ammoniacal medium. The precipitate R gave a coloured solution (S), when treated with H<sub>2</sub>O<sub>2</sub> in an aqueous NaOH medium.

- 1. The precipitate P contains
  - $(1) \text{ Pb}^{2+}$
- $(2) \text{ Hg}_2^{2+}$
- $(3) Ag^{\oplus}$
- $(4) \text{ Hg}^{2+}$
- 2. The coloured solution S contains
  - (1)  $Fe_2(SO_4)_3$
- (2) CuSO<sub>4</sub>
- (3)  $ZnSO_4$
- (4) Na<sub>2</sub>CrO<sub>4</sub>

(JEE Advanced 2013)

## **Numerical Value Type**

1. Among PbS, CuS, HgS, MnS, Ag<sub>2</sub>S, NiS, CoS, Bi<sub>2</sub>S<sub>3</sub> and SnS<sub>2</sub>, the total number of BLACK coloured sulphides is

(JEE Advanced 2014)

## **Answers Key**

**161.** (1)

**162.** (3)

#### **EXERCISES** Single Correct Answer Type 1.(2) **2.** (2) **3.** (3) **4.** (4) **5.** (2) **9.** (1) **7.** (1) **8.** (1) **10.** (3) **6.** (1) **13.** (3) **14.** (2) 15. (4) **11.** (1) **12.** (1) **16.** (2) **17.** (2) **18.** (2) **19.** (2) **20.** (4) **23.** (1) **24.** (3) **25.** (3) 22. (4) **21.** (2) **27.** (2) **28.** (4) **29.** (4) **30.** (1) **26.** (2) **32.** (3) 33. (4) **34.** (4) **35.** (3) **31.** (3) **40.** (2) **37.** (2) 38. (4) **39.** (3) **36.** (1) **43.** (2) **45.** (1) **42.** (4) **44.** (1) **41.** (4) **48.** (1) **49.** (3) **50.** (3) 47. (4) **46.** (1) **53.** (1) **54.** (3) **55.** (1) **52.** (2) **51.** (2) **58.** (2) **59.** (3) **60.** (4) **57.** (2) **56.** (4) **64.** (2) **65.** (4) **63.** (1) **62.** (1) **61.** (1) **69.** (4) **70.** (2) **68.** (2) **67.** (4) **66.** (3) **75.** (4)

**74.** (2)

**73.** (3)

**72.** (1)

**71.** (2)

80.(2) **76.** (3) 77.(3) **79.** (3) **78.** (2) **85.** (1) 84. (4) **81.** (3) **82.** (3) **83.** (3) 90. (4) **89.** (1) **86.** (3) **87.** (3) **88.** (3) **95.**(1) **94.** (3) 91. (4) **92.** (3) 93. (4) 100. (4) **99.** (3) **96.** (3) **97.** (3) **98.** (4) 105. (4) **104.** (1) **101.** (3) **102.** (3) **103.** (1) **110.** (1) 109. (2) **106.** (4) **107.** (4) **108.** (1) **115.** (2) **114.** (2) **113.** (1) **112.** (3) **111.** (3) **120.** (1) **118.** (4) **119.** (1) **117.** (2) **116.** (2) **125.** (4) 124. (4) **123.** (1) 121. (4) **122.** (1) **130.** (3) **129.** (2) **128.** (4) **127.** (4) **126.** (1) **135.** (2) **134.** (3) **133.** (2) **131.** (2) **132.** (1) 140.(4) **139.** (3) **138.** (1) **136.**(1) **137.** (2) 145. (4) **144.** (1) **143**. (4) **142.** (1) **141.** (3) **150.** (1) **149.** (3) **148.** (2) 147.(2) 146.(2) 155.(2) **154.** (1) **153.** (1) **151.** (2) **152.** (1) **160.** (1) **159.** (3) **158.** (4) 157. (4) **156.** (3)

correct Ans	swers Type	
Mitiple Correct Ans		
zi 2.)	<b>2.</b> (1, 3, 4)	<b>3.</b> (1, 2, 3)
$\frac{1}{4}$ , $\frac{1}{2}$ , $\frac{2}{3}$ , $\frac{2}{3}$	<b>5.</b> (2, 3)	<b>6.</b> (3, 4)
4.(2, 3, 3)	<b>8.</b> (3, 4)	<b>9.</b> (1, 2, 3)
$\frac{4}{1}, (1, 2, 3)$ $\frac{1}{1}, (1, 2, 4)$	<b>11.</b> (1, 2, 3)	<b>12.</b> (1, 2, 3)
$\frac{1,(1,2,4)}{10,(1,2,3)}$	<b>14.</b> (1, 2, 4)	<b>15.</b> (1, 2, 3)
1 (1, 2, -)	<b>17.</b> (1, 3, 4)	<b>18.</b> (1,2,3,4)
	<b>20.</b> (1, 2)	<b>21.</b> (1, 2, 4)
0 (1 4,5)	<b>23.</b> (2, 3)	<b>24.</b> (1, 2, 4)
. (2. 3, 4)	<b>26.</b> (2, 3, 4)	<b>27.</b> (1, 2) <b>27.</b> (3, 4)
15 (1,2,3,4)	<b>29.</b> (1, 3)	
18 (1, 2, 4)	<b>32.</b> (1, 2)	<b>30.</b> (1, 3, 4)
31. (1, 2, 3)	<b>35.</b> (1, 2)	<b>33.</b> (1, 2, 3)
14. (3, 4)	` '	<b>36.</b> (2, 4)
37. (3, 4)	<b>38.</b> (1, 3, 4)	<b>39.</b> (1, 3, 4)
40.(1, 2, 4)	<b>41.</b> (1, 2, 3)	<b>42.</b> (1, 2, 3)
43.(1,3)	<b>44.</b> (1, 2, 3)	<b>45.</b> (2, 3, 4)
46. (2, 3, 4)	<b>47.</b> (1, 2)	<b>48.</b> (3, 4)
49. (1, 2, 3)	<b>50.</b> (1, 2, 3)	<b>51.</b> (1, 2)
52.(1,2)	<b>53.</b> (2, 3)	<b>54.</b> (1, 3)
55. (2, 3)	<b>56.</b> (1, 3, 4)	<b>57.</b> (1,2,3,4)
<b>58.</b> (1, 3, 4)	<b>59.</b> (1, 2, 3)	<b>60.</b> (1, 2, 3)
61.(1,4)	<b>62.</b> (1, 3)	<b>63.</b> (3, 4)
64.(1,2,3)	<b>65.</b> (1, 3, 4)	<b>66.</b> (1, 4)
67.(1,3)	<b>68.</b> (1, 3, 4)	<b>69.</b> (1, 2)
70. $(1, 2, 3, 4)$	<b>71.</b> (2, 3)	<b>72.</b> (1, 3, 4)
<b>73.</b> (1, 2)	<b>74.</b> (1, 3, 4)	<b>75.</b> (1,2,3,4)
<b>76.</b> (1, 2, 3)	<b>77.</b> (2, 3)	<b>78.</b> (1, 3)
<b>79.</b> (1,2,3,4)	<b>80.</b> (1,2,3,4)	<b>81.</b> (1, 2, 3)
<b>82.</b> (2, 3, 4)	<b>83.</b> (1, 2, 3)	<b>84.</b> (1,2,3,4)
<b>85.</b> (1, 3, 4)	<b>86.</b> (1, 2, 4)	<b>87.</b> (1, 2, 4)

## linked Comprehension Type

88. (1,2,3,4)

**89.** (1, 2)

1. (3) 6. (2) 11. (2) 16. (4) 21. (2) 26. (2) 31. (1) 36. (3)	2. (1) 7. (1) 12. (2) 17. (1) 22. (2) 27. (1) 32. (2) 37. (3)	3. (2) 8. (2) 13. (1) 18. (3) 23. (2) 28. (1) 33. (3) 38. (2) 43. (3)	4. (2) 9. (3) 14. (4) 19. (3) 24. (2) 29. (2) 34. (2) 39. (1) 44. (2)	5. (3) 10. (1) 15. (3) 20. (2) 25. (2) 30. (3) 35. (2) 40. (3) 45. (1)
<b>26.</b> (2) <b>31.</b> (1)	<b>27.</b> (1) <b>32.</b> (2)	<b>28.</b> (1) <b>33.</b> (3)	<b>34.</b> (2) <b>39.</b> (1)	<b>35.</b> (2) <b>40.</b> (3)

#### **Matrix Match Type**

				d.	e.	1.
Q.No.	a.	b.	c.	р	r	_
1.	s	q	P	q, s	_	_
2.	p, r	p	p, s	S	_	_
2	a	r	P			

		Qua	litative Inc	organic Salt A	nalysis 8	3.67
4.	q	r	s	s	р	_
5.	r, s, t	S	p, s	S	-	_
6.	r	S	p	q	_	_
7.	p, q, s	S	p, s	r, s	_	_
8.	s	r	q	р	_	_
9.	q, s	r, s	p, s	q, s	_	_
10.	р	p,s	r	q,r	_	_
11.	p, q, r, s	p, q	p, q, r	q, r, s	-	-
12.	p, q, r	q, r, s	p, q	p, s	-	-
13.	p, r	q, r, s	q, r, s	p, q, r	_	_
14.	s	r	q	р	_	_
15.	q, r	p	p, s	r	_	_
16.	p, s	q, r	p, q	r	_	_
17.	q	р	S	r	_	_
18.	q	р	s	r	_	-
19.	р	q	r	s	t	u
20.	p	q	r	S	t	u
21.	р	q	r		_	_
22.	I-p	II-q	III-r	IV-s	_	-
23.	IV-q	III-r	II-p	I-s		-
24.	ii-p	i-s	iii-q	iv-r	-	
25.	iii-s	i, ii-p,q	iii-r	ii, v-t,	iv-p	
26.	ii-p	iii-s	i-q	iv-r		

#### **Numerical Value Type**

<b>1.</b> (2)	<b>2.</b> (3)	<b>3.</b> (4)	<b>4.</b> (5)	<b>5.</b> (2)
<b>6.</b> (2)	<b>7.</b> (2)	<b>8.</b> (6)	<b>9.</b> (3)	<b>10.</b> (1)
11. (3)	12. (4)	<b>13.</b> (10)	<b>14.</b> (1)	<b>15.</b> (3)

#### **ARCHIVES**

#### JEE Main

#### Single Correct Answer Type

<b>1.</b> (1)	<b>2.</b> (1)	<b>3.</b> (1)	<b>4.</b> (1)	<b>5.</b> (2)
<b>6.</b> (3)	7. (3)	<b>8.</b> (3)	<b>9.</b> (4)	<b>10.</b> (2)

#### JEE Advanced

#### **Single Correct Answer Type**

<b>1.</b> (1)	<b>2.</b> (4)	<b>3.</b> (4)	<b>4.</b> (2)	<b>5.</b> (1)

## **Multiple Correct Answers Type**

<b>1.</b> (1, 2) <b>2.</b> (1, 3, 4) <b>3.</b> (3, 4) <b>4.</b> (1,	1.	(1, 2)	2. (1	3.4)	3. (3.	4)	4. (	1,3
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## **Linked Comprehension Type**

**1.**(1) **2.**(4)

## **Numerical Value Type**

1.(7)